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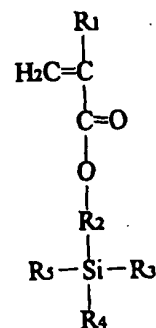
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(54) **COPOLYMER CONTAINING REACTIVE SILYL GROUPS, COMPOSITION CONTAINING THE SAME, AND METHOD OF TREATMENT WITH THE SAME**

(57) A composition of the present invention comprises a copolymer having silyl groups at least one reactive functional group bonded thereto. The copolymer preferably comprises, as one of constitutive monomers, Monomer (A) shown by the following Formula (I):

Formula (I)



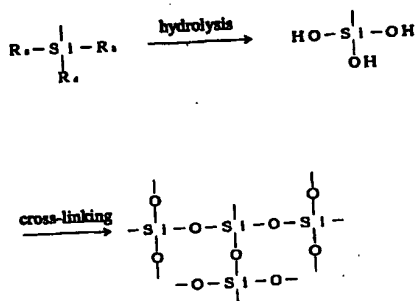
wherein R₁ is hydrogen atom or methyl; R₂ alkylene

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group having 1-6 carbon atoms; and R_3 , R_4 and R_5 each is a reactive functional group which can cross-link molecules of the copolymer by hydrolyzing. Further, the copolymer preferably comprises, as a constitutive monomer, an alkyl (meth)acrylate and a siloxane-containing (meth)acrylate.

The coat-forming method of the present invention comprises hydrolyzing the composition on a material to be treated to cross-link molecules of the copolymer, thereby forming a coat of the cross-linked copolymer having excellent resistance to washing. This coat can exhibit hair nature modifying effect, make-up retention improving effect, and skin-protecting effect. Also, it can impart water-repellency, unsusceptibility to fouling, suitability for sizing and crease resistance to fibers. Further, it can improve skin-cleaning effect, applicability, strippability and coat-strength of a peeling-off type cosmetic pack.

Fig. 1



Description

RELATED APPLICATIONS

- 5 [0001] This application claims the priority of Japanese Patent Application Nos. 9-157675, 9-157676 and 9-157677 filed on May 30, 1997, Japanese Patent Application Nos. 10-55751, 10-55752 and 10-55753 filed on February 20, 1998, Japanese Patent Application Nos. 9-249547 and 9-249548 filed on August 29, 1997, and Japanese Patent Application No. 9-306442 filed on October 20, 1997, which are incorporated herein by reference.

10 FIELD OF THE INVENTION

- [0002] The present invention relates to a copolymer containing reactive silyl groups, a composition comprising the same, and a treating method with the same. Particularly, the present invention relates to: a copolymer, which forms a strong coat of the cross-linked copolymer having resistance to washing on the surface of hair, skin or other materials to
 15 useful effects in the fields of cosmetics and the others such as modifying effect of the nature of hair, improving effect of makeup retention or water-repellent effect; a composition comprising the same; and a treating method with the same.

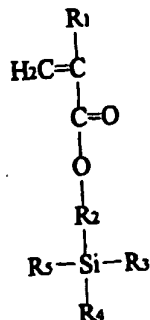
BACKGROUND OF THE INVENTION

- 20 [0003] A numerous film-forming ingredients are used in the fields of cosmetics and the others for the purpose of giving various effects.
 [0004] However, there are very few film-forming ingredients that have an useful effect as a cosmetic ingredient and that maintain the effect against washing with shampoo or detergent.
 [0005] Also, in the other fields, for example, in the field of water-repellents that give water-repellency to fiber, paper
 25 or the other materials, it is expected to improve resistance to washing.

SUMMARY OF THE INVENTION

- [0006] The present invention has been achieved in view of the foregoing problems of the prior art. The first object of
 30 the present invention is to find out a compound that can forms a coat and is to provide a composition comprising the compound, wherein said coat demonstrates useful effects as a cosmetic ingredient, e.g., hair nature modifying effect, make-up retention improving effect of hair colors or make-up cosmetics, or skin-protecting activity and these effects are maintained due to high resistance to washing.
 [0007] Also, the second object of the present invention is to find out a compound that can forms a coat, which is excel-
 35 lent in water-repellency and resistance to washing, on the materials to be treated such as fiber, and is to provide a composition comprising the compound.
 [0008] As a result of the diligent studies performed by the inventors so as to achieve the foregoing objects, it has been found that a strong coat of a cross-linked copolymer that is excellent in resistance to washing can be formed when a
 40 copolymer containing a silyl group that one or more reactive functional group is bonded to (e.g., a monomer having tri-functional silyl group), as a constitutive monomer is cross-linked with hydrolysis on the material to be treated such as hair or skin.
 [0009] Also, it has been ascertained that such cross-linked coat has hair nature modifying effect and skin protecting effect and these effects are maintained without loss even when shampoo is repeated.
 [0010] Also, it has been ascertained that the cross-linked coat formed by such copolymer ameliorates resistance to
 45 washing of make-up cosmetics such as temporary hair color, acidic hair dye, mascara or nail enamel and improves make-up retention.
 [0011] Also, it has been ascertained that a cosmetic pack comprising the copolymer has high skin-cleaning ability and is excellent in applicability, strippability and film strength thereof.
 [0012] Further, the present inventors has found out that a coat which has high water-repellency, unsusceptibility to
 50 fouling and suitability for sizing and is excellent in resistance to washing can be formed even when the copolymer is treated with respect to the other materials such as fiber, paper or glass. Accordingly, the present invention has been accomplished.
 [0013] Namely, a composition of the present invention is characterized by comprising a copolymer containing silyl groups wherein each silyl groups has at least one reactive functional group bonded thereto.
 [0014] In the present invention, the silyl group having at least one reactive functional group bonded thereto is, as men-
 55 tioning in later, that can cross-link molecules of the copolymer by forming siloxane bond Si-O-Si with hydrolysis.
 [0015] Also, in the composition of the present invention, it is preferable that, as one of constitutive monomers, the copolymer comprises Monomer (A) shown by the following Formula (I):

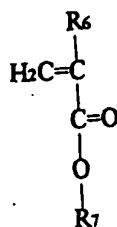
Formula (I)



wherein R_1 is a hydrogen atom or methyl group; R_2 is an alkylene group having 1-6 carbon atoms; and R_3 , R_4 and R_5 each is a reactive functional group which can cross-link molecules of the copolymer hydrolyzing.

[0016] Also, it is preferable that, as one of constitutive monomers, the copolymer further comprises Monomer (B) shown by the following Formula (II):

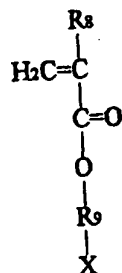
Formula (II)



wherein R_6 is a hydrogen atom or methyl group; and R_7 is an alkyl group having 1-18 carbon atoms.

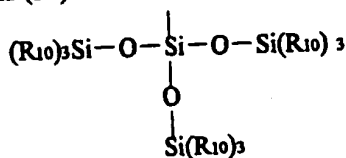
[0017] Also, it is preferable that as one of constitutive monomers, the copolymer further comprises Monomer (C) shown by the following Formula (III):

Formula (III)



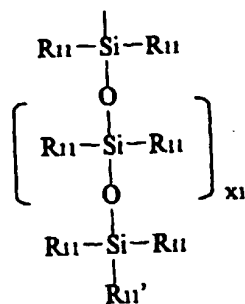
wherein R_8 is a hydrogen atom or methyl group; R_9 is an alkylene group having 1-6 carbon atoms; and X is any of groups shown by the following Formulae (IV) to (VI):

Formula (IV)



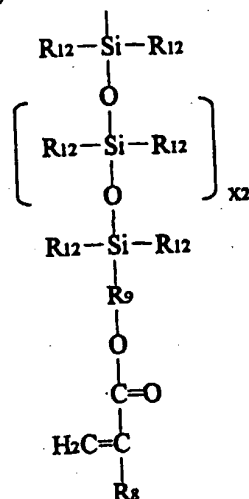
wherein R_{10} is an alkyl group having 1-6 carbon atoms;

Formula (V)



wherein R_{11} and R_{11}' each is an alkyl group having 1-6 carbon atoms; and x_1 is an integer of positive number; and

Formula (VI)



wherein R_8 and R_9 can be the same as defined in Formula (III); R_{12} is an alkyl group having 1-6 carbon atoms; and x_2 is an integer of positive number.

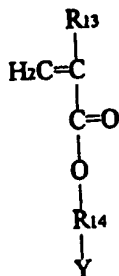
[0018] It is preferable that the percentage of Monomer (A) in the copolymer is 25 to 99 wt%.

[0019] Also, it is preferable that the percentage of Monomer (B) in the copolymer is 1 wt% or more.

[0020] Also, it is preferable that the percentage of Monomer (C) in the copolymer is 1 wt% or more.

[0021] Also, as the constitutive monomers, the copolymer can further comprise Monomer (D) shown by the following Formula (VII):

Formula (VII)



- wherein R_{13} is a hydrogen atom or methyl group; R_{14} is an alkylene group having 1-6 carbon atoms; and Y is a group shown by $-N^+(R_{15})_3$ or $-N(R_{15})_2$, wherein R_{15} is an alkyl group having 1-6 carbon atoms.
- [0022] It is preferable that the percentage of Monomer (D) in the copolymer is within the range of 1 to 100 wt% with respect to a whole amount of Monomers (A), (B) and (C) in the copolymer.
- [0023] Also, it is preferable that R_3 , R_4 and R_5 each is an alkoxy group having 1-6 carbon atoms.
- [0024] A cosmetic for coating in accordance with the present invention is characterized by being a composition comprising any of said copolymers.
- [0025] A cosmetic for modifying hair nature in accordance with the present invention is characterized by being a composition comprising any of said copolymer.
- [0026] A hair color in accordance with the present invention is characterized by being a composition comprising any of said copolymers together with a pigment and/or an acidic dye.
- [0027] A cosmetic in accordance with the present invention is characterized by being a composition comprising any of said copolymers together with a pigment and/or an acidic dye.
- [0028] A make-up cosmetic in accordance with the present invention is characterized by being a composition comprising any of said copolymers together with a pigment and/or an acidic dye.
- [0029] Also, in any of said cosmetics, a siliconized polysaccharide can be further comprised therein.
- [0030] A cosmetic pack in accordance with the present invention is characterized by being a composition comprising any of said copolymers.
- [0031] A water-repellent in accordance with the present invention is characterized by being a composition comprising a copolymer containing at least Monomer (A) shown by Formula (I), Monomer (B) shown by Formula (II) and Monomer (C) shown by Formula (III) as constitutive monomers.
- [0032] In the water-repellent of the present invention, it is preferable that the percentage of Monomer (A) in the copolymer is 25 to 85 wt%. It is also preferable that the percentage of Monomer (B) in the copolymer is 5 wt% or more and the percentage of Monomer (C) in the copolymer is 1 wt% or more.
- [0033] A treatment for fiber in accordance with the present invention is characterized by being a composition comprising a copolymer which containing Monomer (A) shown by Formula (I), Monomer (B) shown by Formula (II), and Monomer (C) shown by Formula (III) as constitutive monomers.
- [0034] In the treatment for fiber of the present invention, it is preferable that the percentage of Monomer (A) in the copolymer is 25 to 85 wt%. It is also preferable that the percentage of Monomer (B) in the copolymer is 5 wt% or more and the percentage of Monomer (C) in the copolymer is 1 wt% or more.
- [0035] A copolymer in accordance with the present invention is characterized by comprising Monomer (A) shown by Formula (I), Monomer (B) shown by Formula (II) and Monomer (C) shown by Formula (III) as constitutive monomers.
- [0036] A copolymer in accordance with the present invention is characterized by comprising Monomer (A) shown by Formula (I), Monomer (B) shown by Formula (II), Monomer (C) shown by Formula (III) and Monomer (D) shown by Formula (VII) as constitutive monomers.
- [0037] In the copolymer of the present invention, R_3 , R_4 and R_5 each is an alkoxy group having 1 to 6 carbon atoms.
- [0038] A coat-forming method in accordance with the present invention is characterized by comprising a step of hydrolyzing said compositions on the materials to be treated to cross-link molecules of the copolymer.
- [0039] In the method of the present invention, it is preferable that the composition is any of said cosmetics and the material to be treated is human hair or epidermis.
- [0040] Also, in the method of the present invention, it is preferable that the composition is any of said water-repellent and the material to be treated is fiber, paper or glass.
- [0041] A method for pack in accordance with the present invention is characterized by comprising steps of: hydrolyzing said cosmetic pack on skin to cross-link molecules of the copolymer; and peeling the cosmetic pack from the skin

after drying.

BRIEF DESCRIPTION OF THE DRAWINGS

5 [0042]

Fig. 1 shows one example of cross-linking reaction of the copolymer in accordance with the present invention.
Figs. 2 to 5 each is a diagram showing NMR spectrum of the copolymer in accordance with one example of the present invention.

10

BEST MODE FOR CARRYING OUT THE INVENTION

[0043] In the following, the embodiment for carrying out the present invention will be explained.

15 [0044] The copolymer comprised in the composition of the present invention contains silyl groups at least one reactive functional group bonded thereto.

[0045] Examples of the copolymer include a copolymer having mono- to tri-functional silyl groups and a copolymer comprising trifunctional silyl groups is preferable in terms of the effect.

[0046] One of the preferable copolymers of the present invention can be a copolymer comprising Monomer (A) shown by Formula (1) as a constitutive monomer.

20 [0047] Monomer (A) is an acrylate or methacrylate comprising a trifunctional silyl group $-\text{SiR}_3\text{R}_4\text{R}_5$. R_1 is a hydrogen atom or methyl group in Formula (I). Also, R_2 is an alkylene group having 1 to 6 carbon atoms and preferably, is propylene group.

25 [0048] R_3 , R_4 , and R_5 each is a reactive functional group, which can cross-link molecules of the copolymer of the present invention due to forming a siloxane bond Si-O-Si by hydrolysis. Examples of such functional group include a hydrogen atom, alkoxy group, halogen atom, acyloxy group and amino group. An alkoxy group having 1 to 6 carbon atoms is preferable in terms of stability of the copolymer, safety of byproduct formed by hydrolysis, reactivity of the cross-linking reaction mentioned later, and the like. Methoxy or ethoxy group is more preferable. Also, R_3 , R_4 , and R_5 each may be the same or different. In the copolymer of the present invention, at least one of Monomer (A) can be used as a constitutive monomer.

30 [0049] Preferably, the copolymer of the present invention comprises the other constitutive monomers along with the monomer containing the reactive silyl group such as Monomer (A) in terms of its effect. Although various monomers may be considered as a constitutive monomer, Monomer (B) shown by the foregoing Formula (II) can be a preferable example.

35 [0050] Monomer (B) is an alkyl acrylate or alkyl methacrylate. In Formula (II), R_6 is a hydrogen atom or methyl group. R_7 is a straight, branched or cyclic alkyl group having 1 to 18 carbon atoms. However, R_7 is preferably an alkyl group having 1 to 6 carbon atoms and, more preferably, methyl group. In the copolymer of the present invention, at least one of the foregoing Monomer (B) can be used as a constitutive monomer.

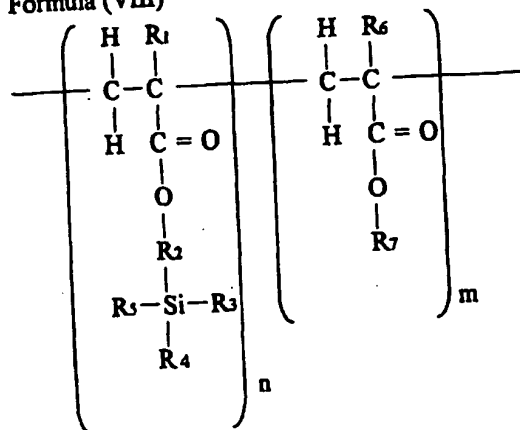
40 [0051] Also, in the copolymer of the present invention, it is preferable to comprise Monomer (C) of the foregoing Formula (III) as a constitutive monomer. Monomer (C) is siloxane-containing (meth)acrylate. R_8 is a hydrogen atom or methyl group in Formula (III). R_9 is an alkylene group having 1 to 6 carbon atoms and, preferably, ethylene, propylene or 2-hydroxypropylene group. X is a siloxane expressed by any of the foregoing Formulae (IV) to (VI). R_{10} , R_{11} , R_{11}' and R_{12} each is a straight or branched alkyl group having 1 to 6 carbon atoms or phenyl group in Formulae (IV) to (VI). Although R_{10} , R_{11} and R_{12} each exist plurally in these formulae, they may be the same or different from each other. Methyl group is preferable as R_{10} , R_{11} and R_{12} . Butyl group is preferable as R_{11}' . A molecular weight of Monomer (C) is 1,000 to 100,000 and, preferably, 2,000 to 20,000 in the case where X is Formula (V) or (VI). Also, in the copolymer of the present invention, at least one of the foregoing Monomer (C) can be used as a constitutive monomer.

45 [0052] The copolymer of the present invention can further comprises amine-containing (meth)acrylate Monomer (D) shown by the foregoing Formula (VII). R_{13} is a hydrogen atom or methyl group in Formula (VII). R_{14} is an alkylene group having 1 to 6 carbon atoms and, preferably, ethylene or propylene group. Y is a group shown by $-\text{N}^+(\text{R}_{15})_3$ or $-\text{N}(\text{R}_{15})_2$, and R_{15} is an alkyl group having 1 to 6 carbon atoms. Also, Y may be a salt whose counter ion is halogen, inorganic acid, organic acid or the like, in the case where Y is the group of $-\text{N}^+(\text{R}_{15})_3$.

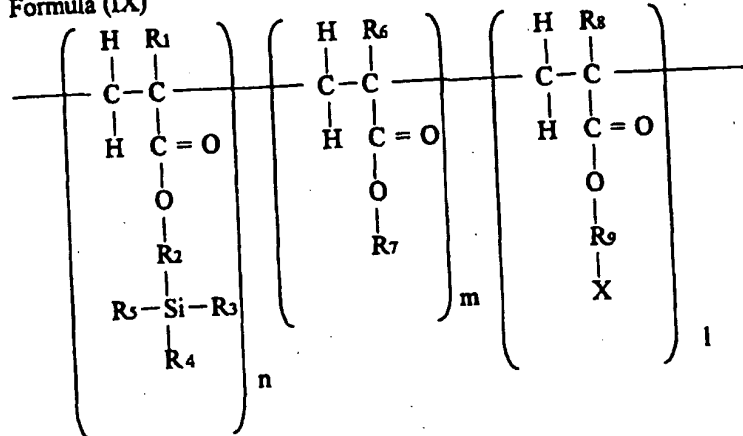
50 [0053] Also, it is possible to comprise Monomer (E) that is not the above-mentioned Monomers (A) to (D) as a constitutive monomer of the copolymer of the present invention within the range that the effect of the present invention is not spoiled.

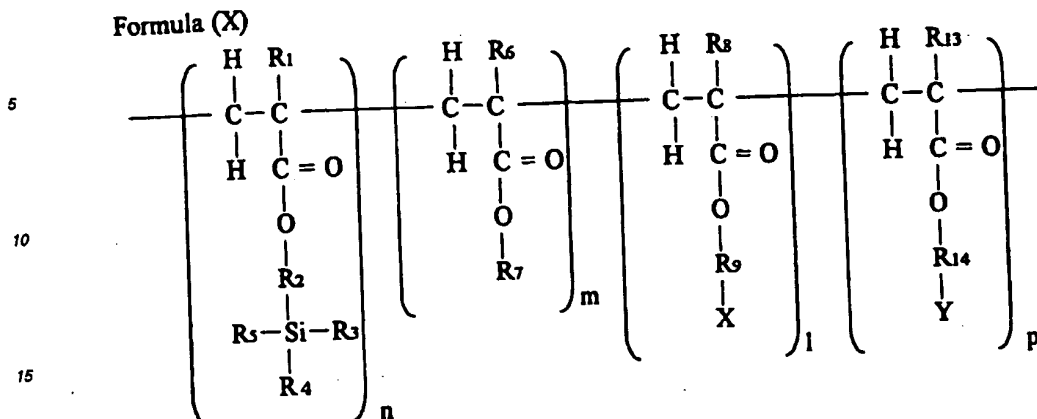
55 [0054] A preferable example of the copolymer comprised in the composition of the present invention can be, for example, a copolymer shown by the following Formulae (VIII), (IX) or (X):

Formula (VIII)



Formula (IX)





wherein $R_1, R_2, R_3, R_4, R_5, R_6, R_7, R_8, R_9, R_{13}, R_{14}, X$ and Y are the same as defined in the above, and n, m, l , and p are molar ratios of Monomers (A), (B), (C) and (D), respectively.

[0055] The copolymer in accordance with the present invention can be obtained by polymerizing the foregoing monomers by means of a known polymerization method such as solution polymerization method, emulsion polymerization method or bulk polymerization method. For example, in case of solution polymerization method, the copolymer of the present invention can be obtained by dissolving each monomer into a solvent with the desired monomer ratio, adding a radical polymerization initiator under nitrogen atmosphere, and heating with stirring.

[0056] As a solvent used in polymerization, it is possible to use any solvent that can dissolve or suspend the monomers and that is an organic solvent which does not comprise water. For example, in addition to alcohol type solvents such as methanol, ethanol, propyl alcohol, isopropyl alcohol or butyl alcohol; hydrocarbon type solvents such as hexane, heptane, octane, isooctane, decane or liquid paraffin; ether type solvents such as dimethyl ether, diethyl ether or tetrahydrofuran; ketone type solvents such as acetone or methyl ethyl ketone; ester type solvents such as methyl acetate, ethyl acetate or butyl acetate; and chloride type solvents such as methylene chloride, chloroform or carbon tetrachloride, dimethylformamide, diethylformamide, dimethylsulfoxide, dioxane or the like can be used. These solvents may be used by mixing two or more of them. In usual, it is preferable to select a solvent having higher boiling point than the starting temperature of polymerization initiator used.

[0057] As the polymerization initiator, it is not limited in particular as long as it has the ability to start radical polymerization. For example, in addition to peroxides such as benzoyl peroxide and azo compounds such as azobisisobutyronitrile or dimethyl 2,2'-azobis(isobutyrate), persulfuric acid type polymerization initiators such as potassium persulfate or ammonium persulfate can be used. Also, the polymerization may be effected with photochemical reaction or radioactive emission even without depending on these polymerization initiators.

[0058] The polymerization temperature is higher than the starting temperature of each polymerization initiator. For example, in case of peroxide type polymerization initiator, the polymerization temperature may be about 70°C in general.

[0059] Although the polymerization time is not restricted in particular, it is 2 to 24 hours in usual. It is desirable to react about 1 day in the case where a polymer having relative high molecule weight is expected to obtain. When the reaction time is too short, unreacted monomer will be left and molecular weight will become relative small.

[0060] The average molecular weight of the copolymer in accordance with the present invention is not restricted in particular, and it can exhibit the expected effect as long as the copolymer has higher polymerization degree than that of an oligomer. However, as will be mentioned later, cross-linking reaction rate will become slow when polymerization degree is low. Also, applicability or workability will be inferior since viscosity becomes higher when polymerization degree is too large. Accordingly, the average molecular weight of the copolymer is preferably about 2,000 to 150,000.

[0061] The copolymer of the present invention comprises the functional silyl groups in its molecule. Therefore, molecules of the copolymer are cross-linked by hydrolyzing, thereby the cross-linked copolymer can be formed. When such cross-linking reaction is conducted on the material to be treated, a coating of the cross-linked copolymer is strongly formed on the surface of the applied portion.

[0062] The forming reaction of such cross-linked coat will be considered as follows. Fig. 1 typically shows the reaction comprising Monomer (A) as a constitutive monomer. The trifunctional silyl group $-\text{SiR}_3\text{R}_4\text{R}_5$ of Monomer (A) is readily hydrolyzed with water, acid, alkali or the like, thereby turning into a trihydroxysilyl group $-\text{Si}(\text{OH})_3$. This trihydroxysilyl

group forms a stable siloxane bond Si-O-Si by reacting with another trihydroxysilyl group. As a result, the copolymer cross-linked (this may refer to the cross-linked copolymer in the present invention) wherein molecules of the copolymer are cross-linked in the form of three-dimensional network, is formed.

[0063] Accordingly, when the copolymer is hydrolyzed on the material to be treated, cross-linking occurs on its applied portion, thereby the cross-linked copolymer can be strongly coated on the surface of the material to be treated in network state. However, when the cross-linked copolymer synthesized in advance, is tried to apply on the material to be treated without cross-linking reaction on the material to be treated, it is very difficult to apply such cross-linked copolymer because the cross-linked copolymer becomes a gel or plastic.

[0064] A method for forming the cross-linked coat with the copolymer of the present invention is characterized in that a composition of the present invention is hydrolyzed on the material to be treated to cross-link molecules of the copolymer. In the present invention, human hair or human epidermis such as skin, nail, eyelashes, eyebrow or the like is preferable as the material to be treated. Also, materials such as fiber, paper or glass can be treated.

[0065] As a method for cross-linking, a reaction with water, acid, or alkali or a reaction with heat can be used. Specifically, after applying the composition of the present invention on the material to be treated, the composition is hydrolyzed to cross-link by bringing the applied portion into contact with water (water vapor or the like may be accepted), acid or alkali or by heating the applied portion. Also, hydrolysis and cross-linking may be conducted by applying the composition on the material treated with water, acid or alkali in advance. Also, the method to apply immediately after water, acid or alkali is mixed with the composition of the present invention may be considered. Generally, however, it is preferable to apply the composition and water, acid, alkali or the like separately. In the case where the composition of the present invention is used as a cosmetic pack, the method to apply immediately after water, acid or alkali is mixed with the composition of the present invention is preferable in terms of strippability. The reaction with water, acid or alkali may be effected with heating. However, it is sufficient to treat at room temperature in usual. Also, it is possible to cross-link naturally with moisture in the atmosphere without bringing the applied portion into contact with acid, water or alkali, when the advance of cross-linking reaction may be slow moving. In any case, instruments such as a brush, a comb, a hair brush or a spray can be used properly as the occasion demands so as to apply and treat the composition uniformly.

[0066] An acid and alkali used in the coat-forming method of the present invention are not limited in particular, as long as they can cross-link the copolymers by hydrolysis. An organic or inorganic acid and alkali can be used therefor. One or more of these acids and alkalis may be used, and also the mixture thereof with water may be used.

[0067] The composition in accordance with the present invention is characterized by comprising the above-mentioned copolymer as an indispensable ingredient. A preferable embodiment of the composition can be a non-aqueous composition containing said copolymer.

[0068] The non-aqueous composition can be, for example, a composition wherein the copolymer is dissolved or dispersed in an organic solvent. Examples of the organic solvent include aliphatic hydrocarbons, aromatic hydrocarbons, aliphatic mono- to tetra-valent alcohols having 1 to 4 carbon atoms, cellosolve type solvents such as ethylcellosolve or butylcellosolve, dioxane, methyl acetate or diformamide. Among these solvents, aliphatic mono- to di-valent alcohols are preferable as cosmetic ingredients. Examples thereof include methanol, ethanol, isopropanol and propylene glycol. In particular, ethanol or isopropanol is preferable in terms of safety.

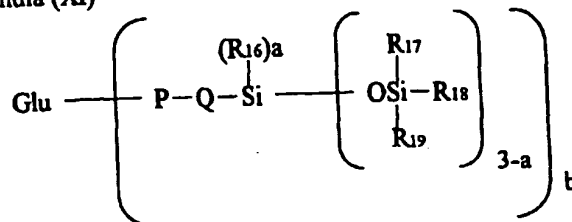
[0069] In the case where the composition of the present invention is a moisture containing composition, it is preferable to prepare the composition wherein it is applied because the cross-linking reaction will occur in the product. Such moisture containing composition also belongs to the category of the present invention.

[0070] A preparation form of the composition in accordance with the present invention is not limited in particular, and any form can be used as long as the effect of the present invention can be exhibited. For example, it can be liquid lotion, milky lotion, cream, gel, mist, spray, aerosol, mousse and the like.

[0071] The other ingredients can be comprised into the composition of the present invention within the range that the effect of the present invention is not spoiled. For example, ingredients comprised in cosmetics normally such as surfactants, humectants, ultraviolet protectors, pH adjusters, antiseptics, antioxidants, chelating agents, thickening agents, film-forming ingredients, oily components, polymers or propellants can be used. It is preferable that water, acid or alkali is comprised in another composition excluding the copolymer. However, it is possible to comprise water, acid or alkali into the composition containing the copolymer of the present invention as mentioned in the above, as long as they are applied to the material to be treated immediately after its preparation.

[0072] In the case where the other film-forming ingredients are comprised into the composition along with the copolymer of the present invention, a preferable film-forming ingredient can be the siliconized polysaccharide shown by Formula (XI):

Formula (XI)

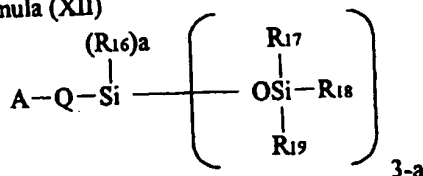


wherein Glu is a sugar residue of a polysaccharide; P is a divalent group for bonding; Q is a divalent aliphatic group; R₁₆ is a monovalent organic group having 1-8 carbon atoms; and R₁₇, R₁₈, and R₁₉ each is a monovalent organic group having 1-8 carbon atoms or a siloxy group shown by —OSiR₂₀R₂₁R₂₂, wherein R₂₀, R₂₁ and R₂₂ each is a monovalent organic group having 1-8 carbon atoms; and a is 0, 1 or 2, and b is an integer of positive number.

[0073] In Formula (XI), Glu is a sugar residue of a polysaccharide. As for such polysaccharide, known various polysaccharides can be used. For example, in addition to cellulose, hemicellulose, gum arabic, tragacanth gum, tamarind gum, pectin, starch, mannan, guar gum, locust bean gum, quince seed gum, alginic acid, carrageenan, agar, xanthan gum, dextran, pullulan, chitin, chitosan, hyaluronic acid and chondroitin sulfate, a derivative of these polysaccharides such as polysaccharide derivatives that is effected by carboxymethylation, sulfation, phosphorylation, methylation, ethylation, addition of an alkylene oxide such as ethylene oxide or propylene oxide, acylation, cationization, or lowering of molecular weight can be used. Among them, ethylcellulose or pullulan is preferable and pullulan is more preferable. In the present invention, though an average molecular weight of the polysaccharide is different according to the kind of the polysaccharide, it is preferably about 1,000 to 5,000,000 in general.

[0074] These polysaccharides have at least one of reactive functional groups such as a hydroxyl or carboxyl group according to the kinds thereof. The divalent group for bonding shown by P is a group derived from A, which is formed by reacting the reactive functional group of the polysaccharide with a silicone compound shown by the following Formula (XII):

Formula (XII)



wherein Q, R₁₆, R₁₇, R₁₈, R₁₉ and a are the same as defined in Formula (XI), and A is a functional group that can react with a reactive functional group of a polysaccharide. For example, isocyanate, epoxy, vinyl, acryloyl, methacryloyl, amino, imino, hydroxyl, carboxyl, mercapto group or the like can be used as A.

[0075] In the reaction between such silicone compound and polysaccharide, known methods such as the method described in Japanese Unexamined Patent Publication No. 8-134103, can be used.

[0076] Example of P include carbamoyl group, —CH₂CH(OH)—, carbonyl group, amino group and ether group. Among them, a carbamoyl group —CONH—, which is formed by reaction of the compound of Formula (XII) wherein A is isocyanate group (O=C=N—) with a hydroxyl group of the polysaccharide, is preferable. The sugar residue of the polysaccharide in this case represents the rest of the polysaccharide excluding the hydrogen atom of the hydroxyl group reacting with the isocyanate group. Also, in the other reaction, the definition of a sugar residue of a polysaccharide is according thereto.

[0077] As for the divalent aliphatic group shown by Q, alkylene group, alkylene group comprising oxygen atom, nitrogen atom, sulfur atom or the like in main chain, alkylene group comprising an arylene group such as phenylene group in main chain, and alkylene group comprising carbonyloxy group or oxycarbonyl group in main chain can be used. These divalent aliphatic groups can have a substituent such as hydroxy, alkoxy, alkyl group or the like, and the terminal atom of the aliphatic group may be a hetero atom such as oxygen atom, nitrogen atom or sulfur atom. Q can be —(CH₂)₂—, —(CH₂)₃—, —(CH₂)₄—, —(CH₂)₅—, —(CH₂)₆—, —(CH₂CH(CH₃))—, —(CH₂)₂O(CH₂)₃—, —CH₂CH(OH)—CH₂— or the like. Propylene group shown by —(CH₂)₃— is preferable.

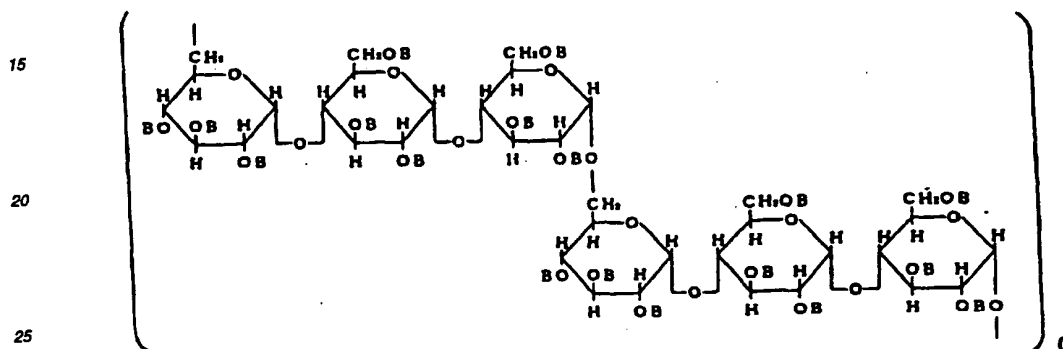
[0078] In Formula (XI), the monovalent organic group having 1-8 carbon atoms shown in R₁₆, R₁₇, R₁₈, R₁₉, R₂₀, R₂₁

and R_{22} , can be an alkyl group such as methyl, ethyl, propyl or butyl group; a cycloalkyl group such as cyclopentyl or cyclohexyl group; an aryl group such as phenyl group; an aralkyl group such as benzyl group; an alkenyl group such as vinyl or allyl group, an fluorinated alkyl group such as 3,3,3-trifluoropropyl group; or the like can be listed. Alkyl group is preferable as such organic group, and methyl group is more preferable.

- 5 [0079] Also, each of R_{17} , R_{18} and R_{19} may be a siloxy group shown by $-\text{OSi}R_{20}R_{21}R_{22}$. Examples of the siloxy group include a trimethylsiloxy, ethyldimethylsiloxy, phenyldimethylsiloxy, vinyltrimethylsiloxy and 3,3,3-trifluoropropyldimethylsiloxy group. Also, R_{16} , R_{17} , R_{18} , R_{19} , R_{20} , R_{21} and R_{22} may be the same or different each other. In the siliconized polysaccharide of the present invention, it is preferable that $a=0$ and R_{17} , R_{18} and R_{19} each is methyl group.

- 10 [0080] In the present invention, more preferable siliconized polysaccharide may be a siliconized pullulan shown by the following Formula (XIII):

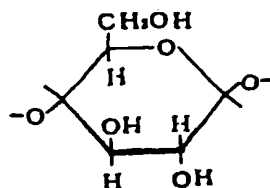
Formula (XIII)



wherein B is a hydrogen atom or a group shown by $-\text{CONH}(\text{CH}_2)_3\text{Si}[\text{OSi}(\text{CH}_3)_3]$ and its substitution degree is 0.5-2.5; and c is a number from 100 to 20,000.

- 30 [0081] In the present invention, the substitution degree of the siliconized polysaccharide represents an average number of the silicone compound bonding to one unit of constituent sugar of the polysaccharide. For example, the substitution degree of the above-mentioned siliconized pullulan indicates the average number of the substituent $-\text{CONH}(\text{CH}_2)_3\text{Si}[\text{OSi}(\text{CH}_3)_3]$ bonding to the base unit of pullulan shown by the following Formula (XIV):

Formula (XIV)



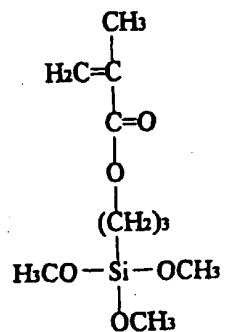
- 50 [0082] Hair nature modifying effect, damaged hair recovering effect, resistance to shampoo, coloring retention effect or the like can be improved by using the copolymer containing reactive silyl groups together with the siliconized polysaccharide. Further, flaking at the time when the composition is repeatedly applied can be inhibited.

- 55 [0083] In the case of compounding the siliconized polysaccharide, when the siliconized polysaccharide dissolving into a solvent such as a silicone oil having low molecular weight or light isoparaffin is used, facility for compounding and feeling of use at the application time can be ameliorated. As for the silicone oil having low molecular weight, linear dimethyl polysiloxane having 2-7 carbon atoms or cyclic dimethyl polysiloxane having 3-7 carbon atoms is preferable. Although an amount of the siliconized polysaccharide in the composition is not restricted in particular, it is 0.01 to 20 wt% in general and, preferably, 0.2 to 10wt%.

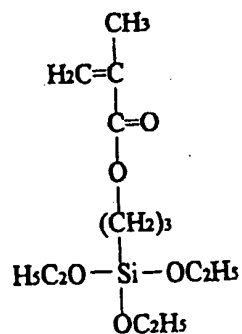
- [0084] In the following, the effect of the composition in accordance with the present invention will be described in

detail. Structures of each monomer used in the following are shown below. Also, the compounding amount is wt% unless otherwise stated.

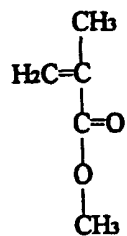
Monomer A1:



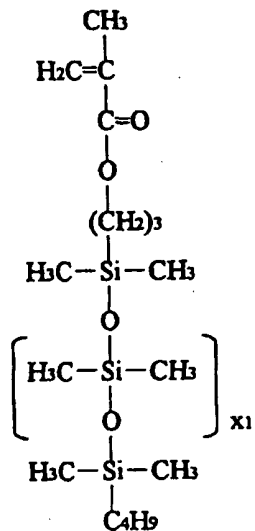
Monomer A2:



Monomer B1:



Monomer C1 (molecular weight 422) and Monomer C2 (molecular weight 12,000):



Monomer C3 (molecular weight 5,000):

5

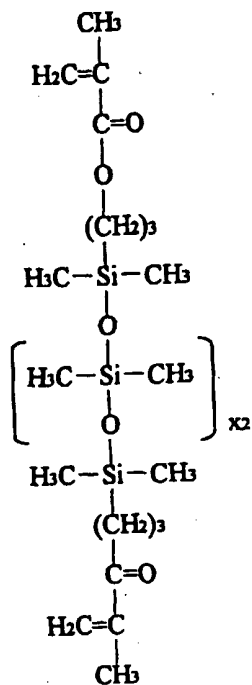
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Monomer C4 :

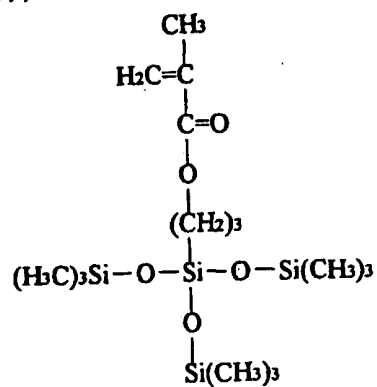
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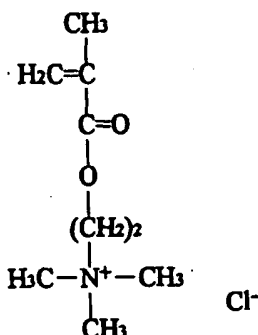
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Monomer D1:



(Cosmetics for Hair Coating)

[0085] A lot of people are not satisfied with respect to their own hairs. For example, the people who have soft hair desire to give tension and hardness to their hair. A lot of hair treatment preparations and hair styling preparations has been developed.

[0086] Also, irrespective of age or sex, coloring of hair according to their own taste has been conducted in usual so as to get rid of discontent concerning the colors of their own hair. This can be considered that the spread of temporary hair colors such as color spray and semipermanent hair color such as acidic hair color that can easily color hair without damaging, largely influenced thereto.

[0087] However, any of such conventional hair treatment or hair styling preparations are effective in nothing but temporary. Because swimming, bathing or shampoo washes off them, the effects are lost. Accordingly, as the nature of hair can not be improved fundamentally even when such preparations are used, it is necessary to continuously use such hair cosmetic preparations every day. Further, there is very few hair cosmetic preparations that can exhibit satisfactory effect.

[0088] Also, as the color of hair by temporary hair color or acidic hair color is easily washed off by shampoo or the like, it is desired to maintain its coloring retention.

[0089] Therefore, the effect when the composition comprising a copolymer of the present invention was treated on hair, was studied.

Test Example 1-1

i) Synthesis of Copolymer

45 Copolymer 1-1

[0090] 2.0g (8mmol) of 3-methacryloxypropyltrimethoxysilane (Monomer A1) and 8.0g (80mmol) of methyl methacrylate (Monomer B1) were dissolved into 100ml of ethanol and the mixture was heated with stirring under nitrogen gas stream for 1 hour at 70°C. 0.05g of potassium persulfate was added to the solution and the mixture was reacted over

50 night. The reaction mixture was cooled down to room temperature and concentrated under a vacuum. The residue was dissolved into 10ml of ethanol and the solution was added to 500ml of n-hexane. The deposits were collected to obtain the aimed copolymer.

[0091] In the NMR spectral data (solvent CDCl_3 or $\text{DMSO}-d_6$) of the resulting copolymer, a peak of hydrogen atom of $\text{CH}_2=\text{C}$ derived from a monomer used as a starting material, that the peak should be observed at 6-7 ppm or near, was not observed. As a result, generation of copolymer was confirmed. Also, in the present invention, generation of the

55 copolymers was confirmed in the similar manner.

Copolymer 1-2

[0092] In the similar manner to Copolymer 1-1, except for using 4.0g (16mmol) of 3-methacryloxypropyltrimethoxysilane and 8.0g (80mmol) of methyl methacrylate, the aimed copolymer was obtained.

Copolymer 1-3

[0093] In the similar manner to Copolymer 1-1, except for using 8.0g (32mmol) of 3-methacryloxypropyltrimethoxysilane and 4.0g (40mmol) of methyl methacrylate, the aimed copolymer was obtained.

Copolymer 1-4

[0094] In the similar manner to Copolymer 1-1, except for using 10.0g (40mmol) of 3-methacryloxypropyltrimethoxysilane and 2.0g (20mmol) of methyl methacrylate, the aimed copolymer was obtained.

Copolymer 1-5

[0095] In the similar manner to Copolymer 1-1, except for using 10.0g (40mmol) of 3-methacryloxypropyltrimethoxysilane and 0.4g (4mmol) of methyl methacrylate, the aimed copolymer was obtained.

Copolymer 1-6

[0096] In the similar manner to Copolymer 1-1, except for using 10.0g (40mmol) of 3-methacryloxypropyltrimethoxysilane, the aimed copolymer was obtained.

ii) Test Method

[0097] Each Copolymers 1-1 to 1-6 was tested by the following method. 3 parts by weight of each copolymer was dissolved into 97 parts by weight of ethanol and the solution which was filled into a spray container was used as a sample.

(Hair nature modifying effect)

[0098] 20 of professional panel were used for evaluating with feelings. Approximately 2g of the spray solution was sprayed on hairs of each panel and the hair was had with a commercially available shampoo. The tension and hardness after drying hair naturally were asked by means of questionnaires and was evaluated by the following standard.

- ⊙ : Among 20 panel, 16 or more answered their own hair had tension and hardness.
- : Among 20 panel, 12 to 15 answered their own hair had tension and hardness.
- △ : Among 20 panel, 6 to 11 answered their own hair had tension and hardness.
- X : Among 20 panel, 0 to 5 answered their own hair had tension and hardness.

(Resistance to shampoo)

[0099] After studying hair nature modifying effect, hair washing with shampoo and drying each was repeated in 3 cycles. The tension and hardness were evaluated with feelings similarly. Evaluation standard was as follows.

- ⊙ : Among 20 panel, 16 or more answered that the effect was maintained and resistance to shampoo was exhibited.
- : Among 20 panel, 12 to 15 answered that the effect was maintained and resistance to shampoo was exhibited.
- △ : Among 20 panel, 6 to 11 answered that the effect was maintained and resistance to shampoo was exhibited.
- X : Among 20 panel, 0 to 5 answered that the effect was maintained and resistance to shampoo was exhibited.

(Flaking)

[0100] In hair nature modifying effect test mentioned above, presence of flaking was judged with visual inspection. Evaluation standard was as follows.

⊙ : Flaking was not observed absolutely.

Δ : Flaking was observed slightly.

X : Flaking was observed clearly.

TABLE 1

Copolymer	Monomer (wt%) A1/B1	Hair nature modifying effect	Resistance to shampoo	Flaking
1-1	20/80	⊙	Δ	⊙
1-2	33/67	⊙	○	⊙
1-3	67/33	⊙	⊙	⊙
1-4	83/17	⊙	⊙	⊙
1-5	96/4	○	○	Δ
1-6	100/0	Δ	Δ	Δ

[0101] From TABLE 1, it is understood that a coating of the cross-linked copolymer containing Monomer A as a constitutive monomer possesses hair nature modifying effect.

[0102] Because resistance to shampoo was not obtained sufficiently, and it was inferior in continuity of hair nature modifying effect in the case where Monomer (A) was too less in the copolymer. On the other hand, both hair nature modifying effect and resistance to shampoo were tended to be lowered and flaking was generated easily, in the case where Monomer (A) was 100%. Therefore, as for monomer composition of the copolymer, Monomer (A) in the copolymer is 25 to 99 wt% and preferably is 40 to 85 wt%.

Test Example 1-2

[0103] The spray prepared in Test Example 1-1 was used as a sample and test for coloring retention was conducted by the following method.

(Coloring retention)

[0104] A commercially available acidic hair color was uniformly applied on a bunch of white human hair. 3 minutes later, the bunch was washed with water and dried naturally. 5g of the colored human hair bunch (control) was taken and approximately 1g of the sample was sprayed thereon. Hair washing with commercially available shampoo and natural drying were repeated ten times with respect to the human hair bunch with or without treatment of the spray. Change of color of thus shampoo-treated human hair bunch with respect to the control that was not treated with shampoo was observed with naked eyes and evaluated.

⊙ : Absolutely no discoloring was occurred.

○ : Almost no discoloring was occurred.

Δ : Discoloring was occurred.

X : Discoloring was occurred remarkably.

TABLE 2

Copolymer	Monomer (wt%) A1/B1	Coloring retention
1-1	20/80	Δ
1-2	33/67	○
1-3	67/33	⊙
1-4	83/17	⊙
1-5	96/4	○
1-6	100/0	Δ

TABLE 2 (continued)

Copolymer	Monomer (wt%) A1/B1	Coloring retention
Nothing (not sprayed)	—	X

[0105] As was understood from TABLE 2, discoloring caused by shampoo was remarkably observed in the case where the hair was not treated with the copolymer. However, in the hair treated with the copolymer, discoloring was inhibited and coloring retention was improved. Therefore, a coat of the cross-linked copolymer in accordance with the present invention possesses coloring retention improving effect when the copolymer was treated on the colored hair. It is understood that the effect is remarkably exhibited in the case where the percentage of Monomer (A) in the copolymer is 25 to 99 wt% and, preferably, 40 to 85 wt%.

Test Example 1-3

[0106] Next, the copolymers that has monomer composition of TABLE 3 were synthesized in the same way as Test Example 1-1 and tested similar to Test Examples 1-1 and 1-2. Also, smoothness and texture were evaluated according to the following method.

(Smoothness)

[0107] Smoothness of the hair after hair nature modifying effect test was asked by means of questionnaires and was evaluated according to the following standard.

- ⊙ : Among 20 panel, 16 or more answered that feeling of use was smooth.
 ○ : Among 20 panel, 12 to 15 answered that feeling of use was smooth.
 △ : Among 20 panel, 6 to 11 answered that feeling of use was smooth.
 X : Among 20 panel, 0 to 5 answered that feeling of use was smooth.

(Texture)

[0108] Texture of the hair after hair nature modifying effect test was asked by means of questionnaires and was evaluated according to the following standard.

- ⊙ : Among 20 panel, 15 or more answered favorable.
 ○ : Among 20 panel, 10 to 14 answered favorable.
 △ : Among 20 panel, 5 to 9 answered favorable.
 X : Among 20 panel, 0 to 5 answered favorable.

TABLE 3

Copolymer	Monomer(wt%)			Hair nature modifying effect	Resistance to shampoo	Flaking	Coloring retention	Smoothness
	A1	B1	C*					
1-7	33	67	—	⊙	○	⊙	○	△
1-8	67	33	—	⊙	⊙	⊙	⊙	△
1-9	50	10	40(C1)	⊙	⊙	⊙	⊙	⊙
1-10	50	10	40(C2)	⊙	⊙	⊙	⊙	⊙
1-11	50	40	10(C3)	⊙	⊙	⊙	⊙	⊙
1-12	60	35	5(C4)	⊙	⊙	⊙	⊙	⊙
1-13	50	—	50(C2)	△	⊙	⊙	⊙	⊙
1-14	25	—	75(C4)	△	○	⊙	○	⊙

* The inside of () represents Monomer (C) used.

[0109] As is understood from TABLE 3, hair nature modifying effect, resistance to shampoo and coloring retention are improved and feeling of use in hair after treatment can be remarkably smoothed by introducing Monomer (C) into the copolymer consisted of Monomers (A) and (B). Also, although hair nature modifying effect was low and the copolymer was difficult to treat due to stickiness in the copolymers 1-13 and 1-14, these copolymers had well property in resistance to shampoo, coloring retention effect and smoothness.

[0110] As shown in the foregoing, the percentage of Monomer (C) in the copolymer is 1 wt% or more and, preferably, 5 wt% or more. It was also indicated that Monomer (B) in the copolymer contributed to hair nature modifying effect and prevention of stickiness of the copolymer and that the percentage of Monomer (B) in the copolymer was 1 wt% or more and, preferably, 10 wt% or more.

TABLE 4

Copolymer	Monomer(wt%)				Hair nature modifying effect	Resistance to shampoo	Coloring retention	Texture
	A2	B1	C4	D1				
1-12	60	35	5	—	⊙	⊙	⊙	Δ
1-15	60	35	5	10	⊙	⊙	⊙	⊙
1-16	60	35	5	20	⊙	○	○	⊙
1-17	60	35	5	50	○	○	○	⊙
1-18	60	35	5	100	Δ	X	X	⊙

[0111] As is understood from TABLE 4, the copolymer consisted of Monomers (A) to (D) can give smoothness, good texture and moist feeling to hair. In the case where the percentage of Monomer (D) was high, hair nature modifying effect, resistance to shampoo and coloring retention tended to be lowered because the hydrophilic nature of the cross-linked coat becomes high. Accordingly, the percentage of Monomer (D) is 1 to 100 wt% and, more preferably, 5 to 50 wt% with respect to the whole amount of Monomers (A) to (C) in the copolymer.

[0112] As mentioned above, by effecting cross-linking reaction after applying the composition comprising the copolymer having reactive silyl groups on hair, tension and hardness are given to the hair. At the same time, an excellent resistance to shampoo can be exhibited, thereby the effect is maintained without loss even after repeating shampoo. Also, feeling of use is not stiffened and flaking does not occurred. Further, in the case where this treatment was effected on colored hair, discoloring at the time of shampoo is inhibited and coloring retention is remarkably improved.

[0113] It can be considered that because cross-linking reaction occur on hair by hydrolyzing the copolymer and the cross-linked coat, which is excellent in resistance to washing, strongly coats the hair in network state, these effects are exhibited.

[0114] Accordingly, the composition of the present invention is useful as a cosmetic for hair coating or for modifying the nature of hair.

[0115] A preferable example of the copolymer to be comprised into the cosmetic for hair coating or for modifying the nature of hair in accordance with the present invention can be shown by Formulas (VIII), (IX) or (X).

[0116] As a monomer composition of the copolymer, the percentage of Monomer (A) in the copolymer is 25 to 99 wt% and, more preferably, 40 to 85 wt%. In the case where Monomer (A) is too little, resistance to shampoo is low and hair nature modifying effect and coloring retention effect may not be sufficiently maintained since the part for cross-linking is few. On the contrary, hair nature modifying effect, coloring retention and resistance to shampoo tend to be lowered in the case where Monomer (A) is too much. Also, flaking is easy to occur. These can be considered that cross-linking reaction is not progressed neatly and a large amount of the unreacted part is remained in the copolymer because the part for cross-linking is too much to be in close state.

[0117] Monomer (B) adjusts the ratio of Monomer (A) and contributes to hair nature modifying effect and water-repellency of the coat of the cross-linked copolymer. Monomer (B) also inhibits flaking. The percentage of Monomer (B) is 1 wt% or more and, more preferably, 10 wt% or more in the copolymer. The percentages of the other monomers are decreased and the copolymer becomes having poor solubility against alcohol type solvents in the case where Monomer (B) is too much. Therefore, the percentage of Monomer (B) is 75 wt% or less and, preferably, 60 wt% or less.

[0118] Monomer (C) has a siloxane part to improve water repellency and resistance to shampoo of the cross-linked coat and to give the hair after treatment smoothness in feeling of use. Monomer (C) can also inhibits flaking. The percentage of Monomer (C) is 1 wt% or more and, preferably, 5 wt% or more in the copolymer of the present invention.

However, when the percentage of Monomer (C) is too large, the percentages of the other monomers become relatively small and resistance to shampoo tends to be poor. Therefore, the percentage of Monomer (C) is 70 wt% or less and, preferably, 60 wt% or less.

[0119] Also, when the copolymer comprising Monomer (D) as a constitutive monomer is treated, good texture can be given to hair and moist feeling of use can be obtained. However, when the percentage of Monomer (D) is too large, water-repellence, resistance to shampoo and the like become poor because hydrophilic nature of the coat becomes high due to amine portion contained in Monomer (D). The percentage of Monomer (D) is 1 to 100 wt% and, preferably, 5 to 50 wt% with respect to a whole amount of Monomers (A) to (C).

[0120] Although a concentration of the copolymer is not restricted in particular, it is preferably 0.1 to 10 wt% and, more preferably, 1 to 5 wt%. When an amount of the copolymer is too little, the sufficient effect can not be obtained at one time treatment. On the contrary, when the amount of the copolymer is too much, applicability, spreadability, feeling of use and the like become inferior and flaking may occur.

[0121] The present inventors further studied about the effect at the time when the copolymer of the present invention and the other film-forming ingredients were used together. As for the film-forming ingredient, siliconized pullulan (substitution degree is 1.7, molecular weight of pullulan used as a starting material is approximately 200,000), which is one of siliconized polysaccharide was used.

Test Example 1-4

[0122] A sample was prepared according to the prescription of TABLE 5 and tested by the following method.

(Hair nature modifying effect)

[0123] 20 of professional panel evaluated with feelings. After approximately 2g of the sample was sprayed on hair of each panel, the hair was washed with water. The question concerned with the tension and hardness of hair after drying naturally were asked by means of questionnaires and was evaluated by the following standard (just after the test). Also, the tension and hardness of hair after repeatedly washing with a commercially available shampoo and natural drying 5 times were also evaluated by the following standard.

- ⊙ : 16 or more answered their own hair had tension and hardness.
- : 12 to 15 answered their own hair had tension and hardness.
- △ : 6 to 11 answered their own hair had tension and hardness.
- X : 0 to 5 answered their own hair had tension and hardness.

(Damaged hair recovering effect)

[0124] 20 of professional panel who had damaged hair were evaluated with feelings. Approximately 2g of the sample was sprayed on hair of each panel and then the hair was washed with water. The question concerned with the touch (smoothness) after natural drying was asked by means of questionnaires and was evaluated by the following standard (just after the test). Also, the touch after repeatedly washing with commercially available shampoo and natural drying 5 times was also evaluated by the following standard.

- ⊙ : 16 or more answered that the touch was smooth and damaged hair recovering effect was obtained.
- : 12 to 15 answered that the touch was smooth and damaged hair recovering effect was obtained.
- △ : 6 to 11 answered that the touch was smooth and damaged hair recovering effect was obtained.
- X : 0 to 5 answered that the touch was smooth and damaged hair recovering effect was obtained.

(Coloring retention)

[0125] Coloring retention had tested according to the method of Test Example 1-2.

(Flaking on repeated application)

[0126] After approximately 2g of the sample was sprayed on the hair of 20 professional panel each, the hair was washed with water and dried naturally. Presence of flaking after repeating the above-mentioned cycle 3 times was judged with visual inspection. Evaluation standard is as follows.

- ⊙ : Flaking was not observed at all.

Δ : Flaking was observed slightly.

X : Flaking was observed clearly.

TABLE 5

Ingredient*	Amount										
	5	-	-	-	-	-	5	-	-	-	-
Copolymer 1-19	5	-	-	-	-	-	5	-	-	-	-
Copolymer 1-20	-	5	-	-	-	-	-	5	-	-	-
Copolymer 1-21	-	-	5	-	-	-	-	-	5	-	-
Copolymer 1-22	-	-	-	5	-	-	-	-	-	5	-
Copolymer 1-23	-	-	-	-	5	-	-	-	-	-	5
Siliconized pullulan	-	-	-	-	-	5	0.5	0.5	0.5	0.5	0.5
Ethanol	35	35	35	35	35	40	35	35	35	35	35
Light isoparaffin	60	60	60	60	60	55	59.5	59.5	59.5	59.5	59.5
Hair nature modifying effect											
Just after test	⊙	⊙	⊙	⊙	Δ	Δ	⊙	⊙	⊙	⊙	○
After 5 times shampoo	○	⊙	⊙	⊙	Δ	Δ	⊙	⊙	⊙	⊙	○
Damaged hair recovering effect											
Just after test	○	○	○	Δ	○	⊙	⊙	⊙	⊙	⊙	⊙
After 5 times shampoo	Δ	○	○	Δ	○	⊙	⊙	⊙	⊙	⊙	⊙
Coloring retention	○	⊙	⊙	⊙	⊙	Δ	⊙	⊙	⊙	⊙	⊙
Flaking on repeated application	Δ	Δ	Δ	X	Δ	⊙	⊙	⊙	⊙	⊙	⊙

* The monomers (wt%) of each copolymer are as follows.

Copolymer 1-19 : A2-B1-C3-D1=60-35-5-20

Copolymer 1-20 : A2-B1-C1=50-40-10

Copolymer 1-21 : A2-B1-C2=50-25-25

Copolymer 1-22 : A2-B1=67-33

Copolymer 1-23 : A2-C3=50-50

[0127] As shown in TABLE 5, when the copolymer and siliconized pullulan were used together, hair nature modifying effect and coloring retention effect can be equal to or be improved as compared with the case where the copolymer only is used. Also, the touch could be more smoothed as compared with the case where the copolymer only was used and the effect was remarkable with respect to damaged hair. Also, these effects were maintained even after repeating shampoo. Further, though flaking by repeated application of the copolymer may be occurred in the case where the copolymer only was used, it can be inhibited by using siliconized pullulan together.

TABLE 6

Ingredient	Amount							
	5	5	5	2	2	1	0.1	-
Copolymer 1-19	5	5	5	2	2	1	0.1	-
Siliconized pullulan	-	0.1	0.5	0.5	2	5	5	5
Ethanol	35	35	35	38	39	39	39.9	40
Light isoparaffin	60	59.9	59.5	59.5	59	55	55	55
Hair nature modifying								
Just after test	⊙	⊙	⊙	⊙	⊙	⊙	○	△
After 5 times shampoo	○	⊙	⊙	⊙	⊙	○	△	△
Damaged hair recovering effect								
Just after test	○	○	⊙	⊙	⊙	⊙	⊙	⊙
After 5 times shampoo	△	○	⊙	⊙	⊙	⊙	⊙	⊙
Coloring retention	○	⊙	⊙	⊙	⊙	○	△	X
Flaking on repeated application	△	⊙	⊙	⊙	⊙	⊙	⊙	⊙

[0128] TABLE 6 is the result that the test was conducted as in Test Example 1-1 with changing the ratios of the copolymer and siliconized pullulan. Hair nature modifying effect and coloring retention tends to be lowered in the case where the copolymer is little. On the other hand, hair nature modifying effect, coloring retention and damaged hair recovering effect were not sufficiently improved and flaking on repeated application may occur in the case where siliconized pullulan is little. Accordingly, the ratio between the copolymer and siliconized pullulan by weight is preferably 100 : 1 and, more preferably, 50 : 1-1 : 1.

[0129] As described in the above, by using a copolymer containing reactive silyl groups together with a siliconized polysaccharide, a composition that hair nature modifying effect, coloring retention and damaged hair recovering effect is high and maintained at the time when shampoo is repeated, and flaking on repeated application is little, can be obtained.

[0130] In the case where only the siliconized polysaccharide is used, hair nature modifying effect and coloring retention effect are low as compared with the case where only the copolymer was used. Therefore, it can be considered that these effects are improved by using the siliconized polysaccharide together with, because the siliconized polysaccharide is included into the cross-linked coat, thereby, at the time of forming the cross-linked coat, the cross-linked coat and the siliconized polysaccharide are synergistically contributed.

Examples 1-1 to 1-3 Hair Spray

[0131] The test has been conducted in the same manner as Test Examples 1-1 and 1-2 by using the hair sprays of TABLE 7. Every example was superior to Comparative Example 1-1 in hair nature modifying effect, resistance to shampoo, flaking and coloring retention.

TABLE 7

Ingredient	Example 1-1	Example 1-2	Example 1-3	Comp. Ex. 1-1
(1) Copolymer 1-1	1	3	5	-
(2) Polyvinylpyrrolidone/vinyl acetate copolymer	-	-	-	5
(3) Ethanol	47	45	43	43
(4) POE (40) hydrogenated castor oil	1	1	1	1
(5) Octyl palmitate	1	1	1	1

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TABLE 7 (continued)

Ingredient	Example 1-1	Example 1-2	Example 1-3	Comp. Ex. 1-1
(6) LPG (3.5kg/cm ² at 20°C)	50	50	50	50
(7) Perfume	q.s.	q.s.	q.s.	q.s.
Hair nature modifying effect	○	⊙	⊙	○
Resistance to shampoo	Δ	Δ	Δ	X
Flaking	⊙	⊙	⊙	X
Coloring retention	Δ	Δ	Δ	X

(Manufacturing process)

[0132] The ingredient (1) or (2) was dissolved into the ingredient (3) and the ingredients (4), (5) and (7) were added to the solution. The mixture was filled into an aerosol container and then the ingredient (6) was filled thereto, thereby obtaining a hair spray.

Examples 1-4 to 1-6 Hair Mist

[0133] The test has been conducted in the same manner as Test Examples 1-1 and 1-2 by using the hair sprays of TABLE 8. Every example was superior to Comparative Example 1-2 in hair nature modifying effect, resistance to shampoo, flaking and coloring retention.

TABLE 8

Ingredient	Example 1-4	Example 1-5	Example 1-6	Comp. Ex. 1-2
(1) Copolymer 1-2	1	3	5	-
(2) Polyvinylalcohol/vinyl acetate copolymer	-	-	-	5
(3) Ethanol	97	95	93	93
(4) POE (9) lauryl ether	1	1	1	1
(5) Dimethylpolysiloxane (5cps)	1	1	1	1
(6) Perfume	q.s.	q.s.	q.s.	q.s.
Hair nature modifying effect	⊙	⊙	⊙	○
Resistance to shampoo	○	○	○	X
Flaking	⊙	⊙	⊙	X
Coloring retention	○	○	○	X

(Manufacturing process)

[0134] The ingredient (1) or (2) was dissolved into the ingredient (3). The ingredients (4) to (6) were added to the solution and then the mixture was filled into a container, thereby obtaining a hair mist.

Examples 1-7 to 1-9 Hair Spray

[0135] The test has been conducted in the same manner as Test Examples 1-1 and 1-2 by using the hair sprays of TABLE 9. Every example was superior to Comparative Example 1-3 in hair nature modifying effect, resistance to shampoo, flaking and coloring retention.

TABLE 9

Ingredient	Example 1-7	Example 1-8	Example 1-9	Comp. Ex. 1-3
(1) Copolymer 1-4	1	3	5	-
(2) Polyvinylpyrrolidone/vinyl acetate copolymer	-	-	-	5
(3) Ethanol	54.5	52.5	50.5	50.5
(4) POE (100) hydrogenated castor oil	1	1	1	1
(5) Highly-polymerized dimethyl-polysiloxane (500cps)	0.5	0.5	0.5	0.5
(6) Dimethylpolysiloxane (5cps)	3	3	3	3
(7) LPG (3.5kg/m ² at 20°C)	40	40	40	40
(8) Perfume	q.s.	q.s.	q.s.	q.s.
Hair nature modifying effect	○	⊙	⊙	△
Resistance to shampoo	⊙	⊙	⊙	X
Flaking	⊙	⊙	⊙	△
Coloring retention	⊙	⊙	⊙	X

(Manufacturing process)

[0136] The ingredient (1) or (2) was dissolved into the ingredient (3) and the ingredients (4), (5) and (7) were added to the solution. The mixture and the ingredient (6) were filled into an aerosol container in order and then a hair spray was obtained.

Examples 1-10 to 1-12 Hair Spray

[0137] The test has been conducted in the same manner as Test Examples 1 - 1 and 1-2 by using the hair sprays of TABLE 10. Every example was superior to Comparative Example 1-4 in hair nature modifying effect, resistance to shampoo, flaking, coloring retention and smoothness.

TABLE 10

Ingredient	Example 1-10	Example 1-11	Example 1-12	Comp. Ex. 1-4
(1) Copolymer 1-9	1	-	-	-
(2) Copolymer 1-11	-	1	-	-
(3) Copolymer 1-14	-	-	1	-
(4) Polyvinylpyrrolidone/vinyl acetate copolymer	-	-	-	1
(5) Ethanol	47.0	47.0	47.0	47.0
(6) POE (40) hydrogenated castor oil	1	1	1	1
(7) Octyl palmitate	1	1	1	1
(8) LPG	50	50	50	50
(9) Perfume	q.s.	q.s.	q.s.	q.s.
Hair nature modifying effect	⊙	⊙	⊙	○
Resistance to shampoo	⊙	⊙	⊙	X

TABLE 10 (continued)

Ingredient	Example 1-10	Example 1-11	Example 1-12	Comp. Ex. 1-4
Flaking	⊙	⊙	⊙	X
Coloring retention	○	⊙	⊙	X
Smoothness	⊙	⊙	⊙	X

(Manufacturing process)

[0138] The ingredients (1) to (4) were dissolved into the ingredient (5) and the ingredients (6), (7) and (9) were added to the solution. The mixture and the ingredient (8) were filled into an aerosol container in order and then a hair spray was obtained.

Examples 1-13 to 1-15 Hair Mist

[0139] The test has been conducted in the same manner as Test Examples 1-1 and 1-2 by using the hair mists of TABLE 11. Every example was superior to Comparative Example 1-5 in hair nature modifying effect, resistance to shampoo, flaking, coloring retention and smoothness.

TABLE 11

Ingredient	Example 1-13	Example 1-14	Example 1-15	Comp. Ex. 1-5
(1) Copolymer 1-8	1	-	-	-
(2) Copolymer 1-10	-	1	-	-
(3) Copolymer 1-11	-	-	1	-
(4) Polyvinylalcohol/vinyl acetate copolymer	-	-	-	1
(5) Ethanol	97.0	97.0	97.0	97.0
(6) POE (9) hydrogenated castor oil	1	1	1	1
(7) Dimethylpolysiloxane	1	1	1	1
(8) Perfume	q.s.	q.s.	q.s.	q.s.
Hair nature modifying effect	⊙	⊙	⊙	○
Resistance to shampoo	⊙	⊙	⊙	X
Flaking	⊙	⊙	⊙	X
Coloring retention	○	⊙	⊙	X
Smoothness	⊙	⊙	⊙	X

(Manufacturing process)

[0140] The ingredients (1) to (4) were dissolved into the ingredient (5) and the ingredients (6) to (8) were added to the solution. A hair mist was obtained by filling the mixture into a container.

Example 1-16

[0141] The copolymers 1-24 to 1-26 were synthesized by the following method and tested in the same manner as Test Examples 1-1 and 1-2. As a result, every copolymer had high hair nature modifying effect, resistance to shampoo and coloring retention, and was favorable in feeling of use as shown in TABLE 12. Also, flaking was not observed in every case.

Copolymer 1-24

[0142] 12.0g of Monomer A2 and 6.0g of monomer B1 were dissolved into 100ml of ethanol and the solution was heated with stirring under nitrogen gas stream for 1 hour at 70°C. 0.05g of dimethyl 2,2'-azobis(isobutyrate) was added to the solution and the mixture was reacted over night. The reaction mixture was cooled down to room temperature and was concentrated under a vacuum. The residue was dissolved into 10ml of ethanol and the solution was added to 500ml of n-hexane. The deposit was collected, thereby obtaining the aimed copolymer.

Copolymer 1-25

[0143] In the similar manner to Copolymer 1-24, except for using 10.0g of Monomer A2, 2.0g of Monomer B1, and 1.0g of Monomer D1, the aimed copolymer was obtained.

Copolymer 1-26

[0144] In the similar manner to Copolymer 1-24, except for using 10.0g of Monomer A2, 10.0g of Monomer C4, and 0.5g of Monomer D1, the aimed copolymer was obtained.

TABLE 12

Copolymer	Monomer(wt%)				Hair nature modifying effect	Resistance to shampoo	Coloring retention	Smoothness	Texture
	A2	B1	C4	D1					
1-24	67	-	-	33	⊙	○	○	○	⊙
1-25	77	15	-	8	⊙	⊙	⊙	○	⊙
1-26	49	-	49	2	⊙	⊙	⊙	⊙	⊙

Example 1-17 Hair Spray

[0145]

(1) Copolymer 1-22	5 wt%
(2) Siliconized pullulan	1
(3) Dimethylpolysiloxane (5mPa.s)	5
(4) Ethanol	15
(5) Light isoparaffin	34
(6) LPG (3.5kg/cm ² at 20°C)	40
(7) Perfume	q.s.

(Manufacturing Process)

[0146] Siliconized pullulan was dissolved into light isoparaffin. The ethanol solution of dimethylpolysiloxane, perfume and Copolymer was added thereto. The mixture and LPG were filled into an aerosol container in order, thereby obtaining a hair spray.

[0147] This hair spray could improve hair nature modifying effect, damaged hair recovering effect and resistance to shampoo and inhibit stalling on repeated application as compared with the hair spray that siliconized pullulan was not compounded thereto.

Example 1-18 Hair Mist

[0148]

5

10

15

(1) Copolymer 1-20	3 wt%
(2) Siliconized pullulan	0.1
(3) Stearyltrimethylammonium chloride	0.5
(4) Ethanol	37
(5) Light isoparaffin	49.4
(6) Dimethylpolysiloxane (5mPa.s)	10
(7) Perfume	q.s.

(Manufacturing Process)

20

[0149] Siliconized pullulan was dissolved into light isoparaffin. The ethanol solution of dimethylpolysiloxane, perfume, copolymer and stearyltrimethylammonium chloride was added thereto. A hair mist was obtained by filling the mixture into a spray container.

25

[0150] This hair mist could improve hair nature modifying effect, damaged hair recovering effect and resistance to shampoo and inhibit staking on repeated application as compared with the hair mist that siliconized pullulan was not compounded thereto.

Example 1-19 Hair Coat

30 [0151]

35

40

(1) Copolymer 1-19	3 wt%
(2) Siliconized pullulan	0.5
(3) Stearyltrimethylammonium chloride	0.5
(4) Ethanol	37
(5) Light isoparaffin	19
(6) LPG (3.5kg/cm ² at 20°C)	40
(7) Perfume	q.s.

45

(Manufacturing Process)

50

[0152] Siliconized pullulan was dissolved into light isoparaffin. The ethanol solution of dimethylpolysiloxane, perfume, copolymer and stearyltrimethylammonium chloride was added thereto. The mixture and LPG were filled into an aerosol container in order, thereby obtaining a hair coat.

[0153] This hair coat could improve coloring retention of the hair that was colored with temporary or acidic hair dye, as compared with the hair coat that siliconized pullulan was not compounded thereto.

(Cosmetics for Skin Coating)

55

[0154] A lot of people are suffering from rough skin, nail cracking or dermatopathy caused by water or detergent. In particular, a beautician, the person engaged in medical, a housewife or the like has a serious problem that nail cracking and rough skin are readily to pass into a chronic state due to the repeated cleaning and washing. Also, the people who

have a delicate skin have a problem that barber's itch or the like is easy to occur in shaving.

[0155] In order to protect nails or skin from such external irritations, there is a method for coating the portion.

[0156] Also, in make up cosmetics, as a method for improving its retention, there is a method for coating on the portion where make up cosmetics is applied thereon in advance. For example, a top coat of nail enamel and a cosmetic preparation for coating which is used for putting on mascara or eyebrow are known well.

[0157] However, cosmetic preparations for coating having sufficient effects in water-repellency, resistance to washing, improving effect of make up cosmetics retention or the like have not been obtained.

[0158] Accordingly, the effects in the case where the compositions comprising the copolymer containing reactive silyl groups are treated on a portion excluding hair such as skin or nail were studied.

Test Example 2-1 Skin Protecting Effect

Prescription 2-1:

[0159]

Glyceryl tri-2-ethylhexanoate	1.0 wt%
1,3-Butyleneglycol	1.0
Ethanol	96.0
Copolymer	2.0
Vitamin A acetate	q.s.

[0160] A sample solution was prepared by the above-described prescription 2-1. As a control, a solution using ethanol instead of the copolymer was also prepared in the same way. Each preparation was filled into a spray container severally and skin protecting effect thereof is tested.

(Skin Protecting Effect)

[0161] The sample was sprayed on the portion to be shaved in 20 male panel. After washing the portion to be treated with water, moisture was wiped with a towel. Then, a beard was shaved with a razor and a state of skin roughness after shaving was evaluated. Evaluation standard is as follows.

⊙ : Among 20 panel, 16 or more evaluated that skin roughness was very few.

○ : Among 20 panel, 12 to 15 evaluated that skin roughness was very few.

△ : Among 20 panel, 6 to 11 evaluated that skin roughness was very few.

X : Among 20 panel, 0 to 5 evaluated that skin roughness was very few.

TABLE 13

Copolymer	Monomer (wt%) A1/B1	Skin Protecting Effect
2-1	20/80	△
2-2	33/67	○
2-3	67/33	⊙
2-4	83/17	⊙
2-5	96/4	○
2-6	100/0	△
Nothing (Ethanol)	—	X

[0162] As is clear from TABLE 13, it is understood that the cross-linked coat formed by the copolymer containing Mon-

omer (A) as a constitutive monomer, had skin protecting effect.

[0163] Also, skin protecting effect tended to be lowered in the case where Monomer (A) in the copolymer was too less or too much. Accordingly, it was indicated that the percentage of Monomer (A) was preferably 25 to 99 wt% and, more preferably, 40 to 85 wt%.

Test Example 2-2

[0164] A sample solution was prepared by dissolving 3 parts by weight of a copolymer into 97 parts by weight of ethanol and nail enamel retention thereof was tested. Namely, nails of female panel's both hands were coated with a red nail enamel, which was commercially available. After drying, only the right hand's nails were coated with the sample solution using a brush for nail enamel. After drying, the both hands were washed with water and moisture was wiped with a towel. With respect to the state of nail enamel after 1 week the state of the right hand's nail was evaluated by using the left hand's nail as a control. Flaking was also evaluated. Evaluation standard is as follows.

(Evaluation standard of make retention)

[0165]

- ⊙ : Peeling of nail enamel was not observed at all.
- : Peeling of nail enamel was observed hardly.
- △ : Peeling of nail enamel was observed.
- X : Peeling of nail enamel was observed remarkably.

(Evaluation standard of flaking)

[0166]

- ⊙ : Flaking was not observed at all.
- △ : Flaking was observed slightly.
- X : Flaking was observed clearly.

TABLE 14

Copolymer	Monomer (wt%)	Make Retention		Flaking
		Right hand	Control (left hand)	Right hand
2-1	20/80	△	X	⊙
2-2	33/67	○	X	⊙
2-3	67/33	⊙	X	⊙
2-4	83/17	⊙	X	⊙
2-5	96/4	○	X	△
2-6	100/0	△	X	△

[0167] As is clear from TABLE 14, peeling of nail enamel was remarkable and the color of nail was off in the case where the copolymer was not applied. On the contrary, peeling of nail enamel was inhibited and retention of color was improved in the case where the copolymer was applied over the nail enamel.

[0168] Also, this effect tended to be lowered in the case where Monomer (A) in the copolymer was too less or too much. Accordingly, the percentage of Monomer (A) in the copolymer was preferably 25 to 99 wt% and, more preferably, 40 to 85 wt%.

Test Example 2-3

[0169] Next, the copolymer having the monomer composition of TABLE 15 was tested in the same way as Test Examples 2-1 and 2-2. Also, feeling of use in skin protecting effect test was evaluated according to the following standard.

(Evaluation standard of feeling of use)

[0170]

- 5 ⊙ : Among 20 panel, 16 or more answered that feeling of use was good.
 ○ : Among 20 panel, 12 to 15 answered that feeling of use was good.
 △ : Among 20 panel, 6 to 11 answered that feeling of use was good.
 X : Among 20 panel, 0 to 5 answered that feeling of use was good.

TABLE 15

Copolymer	Monomer(wt%)			Skin Protecting Effect	Feeling of Use
	A2	B1	C*		
2-7	33	67	—	○	○
2-8	50	10	40(C1)	⊙	⊙
2-9	50	10	40(C2)	⊙	⊙
2-10	50	40	10(C3)	⊙	⊙
2-11	60	35	5(C4)	⊙	⊙
2-12	35	55	10(C2)	⊙	⊙
2-13	50	—	50(C2)	⊙	⊙
2-14	25	—	75(C4)	○	⊙

* The inside of () represents Monomer (C) used.

TABLE 16

Copolymer	Monomer(wt%)			Make Retention		Feeling of Use
	A2	B1	C*	Right hand	Left hand (control)	
2-7	33	67	—	○	X	⊙
2-8	50	10	40(C1)	⊙	X	⊙
2-9	50	10	40(C2)	⊙	X	⊙
2-10	50	40	10(C3)	⊙	X	⊙
2-11	60	35	5(C4)	⊙	X	⊙
2-12	35	55	10(C2)	⊙	X	⊙
2-13	50	—	50(C2)	⊙	X	⊙
2-14	25	—	75(C4)	○	X	⊙

* The inside of () represents Monomer (C) used.

50 [0171] As is clear from TABLE 15 and 16, feeling of use could be improved along with skin protecting effect and make retention by introducing Monomer (C). Also, Monomer (C) contributed to inhibition of flaking. Although copolymers 2-13 and 2-14 which were consisted of Monomers (A) and (C) were difficult to treat due to its stickiness, skin protecting effect, improving effect of make retention and feeling of use were fully satisfied.

55 [0172] Consequently, the percentage of Monomer (C) in the copolymer was preferably 1 wt% or more and, more preferably, 5 wt% or more. Also, Monomer (B) in the copolymer contributed to prevention of stickiness of the copolymer. Accordingly, it was indicated that the percentage of Monomer (B) was preferably 1 wt% or more and, more preferably, 10 wt% or more.

[0173] As mentioned above, in the case where nail, skin, eyebrow, eyelashes or the like is coated with comprising the

copolymer containing reactive silyl groups and the cross-linking reaction is effected, due to formation coat which is excellent in water-repellency and resistance to washing and which has no adhesion against the object to be contacted, the coated portion is protected. Also, such protecting effect can be exhibited continuously, since the coat is very hard to come off even when water or detergent is used for washing. Further, feeling of use is not stiffened and no flaking occurs.

[0174] For example, barber's itch can be prevented when the cosmetics for skin of the present invention is used as a preshaving lotion before shaving. Also, in the case where the cosmetics for skin of the present invention is applied over a makeup cosmetic such as nail enamel, its retention is considerably improved.

[0175] Such effect can be considered as follows. When cross-linking occurs in the coated portion, the copolymer forms a cross-linked coating which is excellent in water repellency and resistance to washing and the coated portion was strongly coated with the coat in a network state. Accordingly, the coated portion is uniformly protected.

[0176] Therefore, the composition of the present invention is useful as a cosmetic for skin coating. The cosmetic for skin coating of the present invention can be applied on epidermis except for hair such as nail, eyebrow or eyelashes, in addition to skin.

[0177] A preferred examples of the copolymer to be comprised to the cosmetic for skin coating of the present invention can include the copolymers shown by Formulas (VIII) and (IX).

[0178] As a monomer composition of the copolymer, the percentage of Monomer (A) in the copolymer is preferably 25 to 99 wt% and, more preferably, 40 to 85 wt%. In the case where the percentage of Monomer (A) is too small, water-repellency and resistance to washing is low and effects such as skin protecting action or improvement of makeup retention may not be exhibited sufficiently, since the part for cross-linking reaction is few. On the other hand, when the percentage of Monomer (A) is 100 wt%, skin protecting effect and improving effect of makeup retention tends to be lowered. Also, flaking is easy to occur. This can be considered that cross-linking reaction is not progressed neatly and a large amount of the unreacted part is remained on the copolymer because cross-linking reaction part is too much to be close.

[0179] Monomer (B) adjusts the ratio of Monomer (A). Also, Monomer (B) contributes to water-repellency and inhibits flaking. The percentage of Monomer (B) in the copolymer is 1 wt% or more and, preferably, 10 wt% or more. The percentages of other monomers are lowered and the copolymer becomes to have poor solubility against alcohol type solvent in the case where Monomer (B) is too much. Therefore, the percentage of Monomer (B) is 75 wt% or less and, preferably, 60 wt% or less.

[0180] Monomer (C) has a siloxane part. Accordingly, Monomer (C) can improve water-repellency and resistance to washing of the cross-linked coat and make feeling of use favorable. Also, Monomer (C) can inhibits flaking. The percentage of Monomer (C) is 1 wt% or more and, preferably, 5 wt% or more in the copolymer of the present invention. However, when the percentage of Monomer (C) is too large, the percentages of the other monomers become relatively low and resistance to washing tends to be poor. Therefore, the percentage of Monomer (C) is 70 wt% or less and, preferably, 60 wt% or less.

[0181] Also, when the copolymer, which comprises Monomer (D) as a constitutive monomer along with the above-mentioned Monomers (A) to (C), is used, the percentage of Monomer (D) in the copolymer is 100 wt% or less and, preferably, 50 wt% or less with respect to a whole amount of Monomers (A) to (C). In the case where the percentage of Monomer (D) is too large, water-repellence, resistance to washing and the like become poor because hydrophilic nature of the coat becomes high due to amine portion contained in Monomer (D).

[0182] Although an amount of the copolymer in the cosmetic for skin coating in accordance with the present invention is not restricted in particular, it is preferably 0.1 to 10 wt% and, more preferably, 1 to 5 wt%. In the case where the amount is too less, a sufficient effect can not be obtained at one time treatment. On the contrary, applicability, spreadability and the like may become poor and flaking may occur in the case where the amount is too much.

[0183] As for the cosmetic for skin coating in accordance with the present invention, for example, in addition to hand lotion and preshaving lotion, there can be top coat of nail enamel, a cosmetic for coating over mascara or eyebrow.

[0184] Also, the above-mentioned silicized polysaccharide can use together in the cosmetic for skin coating of the present invention.

Example 2-1 Mascara Coat

[0185]

Polyacrylate emulsion	30 wt%
Solid paraffin	8

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(continued)

Light isoparaffin	10
Sorbitan sesquioleate	4
Ethanol	46
Copolymer 2-4	2
Antiseptic	q.s.
Perfume	q.s.

(Manufacturing Process)

[0186] Each ingredient was mixed at 70°C, successively. The mixture was unified with a homomixer to obtain a mascara coat.

[0187] When the present mascara coat was applied with a brush after applying a commercially-available mascara and dried naturally, retention of mascara was improved.

Example 2-2 Nail Coat

[0188]

Nitrocellulose	10 wt%
Epoxy-denatured phthalic alkyd resin	5
Sucrose benzoate	5
Acetyltriethyl citrate	5
Ethyl acetate	20
Butyl acetate	20
Ethanol	30
Copolymer 2-5	5

(Manufacturing Process)

[0189] Each ingredient was mixed and the mixture was shaken for 1 hour at room temperature to obtain a nail coat.

[0190] When the present nail coat was applied with a brush after applying a commercially-available nail enamel and dried naturally, retention of nail enamel was improved.

Example 2-3 Mascara Coat

[0191]

Polyacrylate emulsion	30 wt%
Solid paraffin	8
Light isoparaffin	10
Sorbitan sesquioleate	4
Ethanol	46
Copolymer 2-8	2

(continued)

Antiseptic	q.s.
Perfume	q.s.

5

(Manufacturing Process)

[0192] Each ingredient was mixed at 70°C, successively and the mixture was unified with a homomixer to obtain a mascara coat.

10 [0193] When the present mascara coat was applied with a brush after applying a commercially-available mascara and dried naturally, retention of mascara was improved and feeling of use thereof was smooth to be very favorable.

Example 2-4 Nail Coat

15 [0194]

20

25

30

Nitrocellulose	10 wt%
Epoxy-denatured phthalic alkyd resin	5
Sucrose benzoate	5
Acetyltriethyl citrate	5
Ethyl acetate	20
Butyl acetate	20
Ethanol	30
Copolymer 2-11	5

(Manufacturing Process)

[0195] Each ingredient was mixed and the mixture was shaken for 1 hour at room temperature to obtain a nail coat.

35 [0196] When the present nail coat was applied with a brush after applying a commercially-available nail enamel and dried naturally, retention of nail enamel was improved. Also, feeling of use thereof was very smooth to be favorable.

(Cosmetics Containing Pigment and/or Acidic Dye)

40 [0197] A pigment or dye is used for various cosmetics as a coloring material.

[0198] Among such cosmetics, a hair color is classified broadly into: a temporary hair color which comprises a pigment as a main coloring ingredient and makes the coloring ingredient adhere only on the surface of the hair (e.g., color stick, color spray or the like); a semipermanent hair color (acidic hair color) which comprises an acidic dye as a main coloring ingredient and make a part of the coloring ingredient penetrate into the inside of hair; and a permanent hair color (oxidation hair color) which comprises an oxidation dye color as a main coloring ingredient and colors to deep part of hair.

[0199] Among these hair colors, though the oxidation hair color can maintain color thereof, it has problems such as hair damage easily caused, eruption or coloring of scalp, and its difficulty on treatment.

50 [0200] On the contrary, though the temporary and semipermanent hair colors do not cause hair damage and skin irritation and can be treated conveniently, there are disadvantages that color retention is poor and the hair colors are easy to come off. Accordingly, it is desired to improve color retention of such temporary or semipermanent hair color.

[0201] In addition to such hair cosmetics, a pigment or dye is an essential ingredient in makeup cosmetics. It is also desired to improve water-repellency and cosmetic retention in such the makeup cosmetics.

55 [0202] Therefore, the effect in the case where the copolymer containing reactive silyl groups was comprised into the cosmetic containing a pigment or acidic dye was studied.

Test Example 3-1

i) Preparation of Sample

5 Prescription 3-1:

[0203]

10

(1) Copolymer	2 or 3 wt%
(2) Carbon black	2
(3) Ethanol	44.8 or 43.8
(4) Beeswax	10
(5) Japanese wax	10
(6) Castor oil	30
(7) POE (20) sesquioleate	1.2
(8) Perfume	q.s.
(9) Antioxidant	q.s.

15

20

25

(Manufacturing Process)

[0204] Oily ingredients and carbon black were added into an ethanol solution of the copolymer, successively. After adding perfume and antioxidant into the mixture, a temporary hair color was obtained by stirring sufficiently.

30

ii) Test Method

[0205] Each sample was applied on white hair and the hair was left for 3 minutes. Then the hair was washed with water and dried naturally. Presence of flaking was evaluated at this time. Thereafter, the hair was washed with a commercially available shampoo and dried naturally, to evaluate coloring retention by visual inspection. Also, a hair color, which comprises ethanol instead of the copolymer, was prepared as a control and tested in the same manner. Evaluation standard is as follows.

35

(Evaluation standard of coloring retention)

40

[0206]

⊙ : Coloring effect was maintained for 7 days or more.

○ : Coloring effect was maintained for 4-6 days.

45

△ : Coloring effect was maintained for 2-3 days.

X : No durability.

(Evaluation standard of flaking)

50

[0207]

⊙ : Flaking was not observed at all.

△ : Flaking was observed slightly.

X : Flaking was observed clearly.

55

TABLE 17

Copolymer	Monomer (wt%)	Coloring Retention		Flaking
		2 wt%	3 wt%	3 wt%
3-1	20/80	△	○	⊙
3-2	33/67	○	⊙	⊙
3-3	67/33	○	⊙	⊙
3-4	83/17	○	⊙	⊙
3-5	96/4	○	⊙	⊙
3-6	100/0	△	○	△
Nothing (Ethanol)	—	X	X	⊙

[0208] As is clear from TABLE 17, it is understood that the temporary hair color which comprises the copolymer is excellent in resistance to washing and is considerably improved in coloring retention as compared with the case that the copolymer is not comprised.

Test Example 3-2

[0209] A liquid acidic hair color was prepared according to the following prescription 3-2 and coloring retention and flaking were tested in the same way as the above-mentioned Test Example 3-1.

Prescription 3-2:

[0210]

Copolymer	2 or 3 wt%
Acidic dye (Natrozole)	1
Ethanol	20.7 or 19.7
Benzyl alcohol	6
Isopropyl alcohol	20
Lactic acid	0.3
Silicone KF-56 (manufactured by Shin-Etsu Chemical Co., Ltd.)	50
Perfume	q.s.
Antioxidant	q.s.

TABLE 18

Copolymer	Monomer (wt%)	Coloring Retention		Flaking
		2 wt%	3 wt%	3 wt%
3-1	20/80	△	○	⊙
3-2	33/67	○	⊙	⊙

TABLE 18 (continued)

Copolymer	Monomer (wt%)	Coloring Retention		Flaking
		2 wt%	3 wt%	3 wt%
3-3	67/33	○	⊙	⊙
3-4	83/17	○	⊙	⊙
3-5	96/4	○	⊙	⊙
3-6	100/0	△	○	△
Nothing (Ethanol)	—	△	△	⊙

[0211] As is clear from TABLE 18, it is understood that an excellent resistance to washing is exhibited and coloring retention is improved even in the case where the copolymer of the present invention is comprised into an acidic hair color.

[0212] Also, in the case where the percentage of Monomer (A) in the copolymer is too small or too large, resistance to washing becomes poor and coloring retention tends to be lowered. Accordingly, the percentage of Monomer (A) in the copolymer is preferably 25 to 99 wt% and, more preferably, 40 to 85 wt%.

Test Example 3-3

[0213] Next, by using the copolymer having a monomer composition of TABLE 21, a temporary and acidic hair color were prepared according to the following prescriptions 3-1 and 3-2, respectively. These hair colors had been tested in the same way as Test Example 3-1. A compounding amount of each copolymer was 2 wt%. Also, in coloring retention test, smoothness and texture after applying the sample, washing with water and natural drying were evaluated according to the evaluation standard of the above-mentioned Test Example 1-3.

TABLE 19

Temporary hair color (prescription 3-1, copolymer 2 wt%)						
Copolymer	Monomer(wt%)			Coloring Retention	Smoothness	Flaking
	A2	B1	C*			
3-7	67	33	—	○	○	⊙
3-8	50	10	40(C1)	⊙	⊙	⊙
3-9	50	10	40(C2)	⊙	⊙	⊙
3-10	50	40	10(C3)	⊙	⊙	⊙
3-11	60	35	5(C4)	⊙	⊙	⊙
3-12	50	—	50(C2)	○	⊙	⊙
3-13	25	—	75(C4)	△	⊙	⊙

* The inside of () represents Monomer (C) used.

TABLE 20

Acidic hair color (prescription 3-2, copolymer 2 wt%)						
Copolymer	Monomer(wt%)			Coloring Retention	Smoothness	Flaking
	A2	B1	C*			
3-7	67	33	—	○	⊙	⊙
3-8	50	10	40(C1)	⊙	⊙	⊙
3-9	50	10	40(C2)	⊙	⊙	⊙
3-10	50	40	10(C3)	⊙	⊙	⊙
3-11	60	35	5(C4)	⊙	⊙	⊙
3-12	50	—	50(C2)	⊙	⊙	⊙
3-13	25	—	75(C4)	○	⊙	⊙

* The inside of () represents Monomer (C) used.

[0214] As is clear from TABLES 19 and 20, along with coloring retention of the hair color, feeling of use of hair after treatment could be improved by introducing Monomer (C) into the copolymer. Although copolymers 3-12 and 3-13 which were consisted of Monomers (A) and (C) were difficult to treat due to its stickiness, coloring retention and smoothness were fully satisfied.

[0215] Consequently, the percentage of Monomer (C) in the composition is preferably 1 wt% or more and, more preferably, 5 wt% or more. Also, Monomer (B) in the copolymer contributed to prevent stickiness of the copolymer. Accordingly, it is indicated that the percentage of Monomer (B) is preferably 1 wt% or more and, more preferably, 10 wt% or more.

TABLE 21

Temporary hair color (prescription 3-1, copolymer 2 wt%)						
Copolymer	Monomer (wt%)				Coloring Retention	Texture
	A2	B1	C4	D1		
3-11	60	35	5	-	⊙	Δ
3-14	60	35	5	10	⊙	⊙
3-15	60	35	5	20	○	⊙
3-16	60	35	5	50	○	⊙
3-17	60	35	5	100	X	⊙

[0216] As is clear from TABLE 21, good texture and moist touch can be given to hair in the case where the copolymer which is consisted of Monomers (A) to (D). Also, when a percentage of Monomer (D) is higher, coloring retention effect tends to be lowered because hydrophilic nature of the cross-linked coat becomes high. This tendency was the same for the acidic hair color. Accordingly, the percentage of Monomer (D) is 1 to 100 wt% and, preferably, 5 to 50 wt% with respect to a whole amount of Monomers (A) to (C) in the composition.

[0217] As mentioned above, in the case where the cosmetics comprising the copolymer containing reactive silyl groups, along with a color material such as pigment or acidic dye, is applied on the hair and the cross-linking reaction is effected, the cosmetic is excellent in water-repellent and resistance to washing and has no adhesion against the object to be contacted, and retention of hair color is remarkably improved. Also feeling of use is not stiffened and no flaking occurs. Also, even in the case where the cosmetic of the present invention is applied as a make up cosmetic, the same effects can be exhibited and makeup retention is considerably improved.

[0218] Such effect can be considered as follows. A cross-linked coat strongly coats the applied portion in network state with enveloping the coloring material such as pigment or acidic dye. Accordingly, a coat excellent in water-repel-

lency and resistance to washing can be formed.

[0219] Therefore, the composition comprising the copolymer containing reactive silyl groups and pigment and/or acidic dye is useful as a cosmetic and, in particular, as a hair color such as temporary or acidic hair color and a make up cosmetic.

5 [0220] Preferred examples of the copolymer to be comprised to such cosmetics can include the copolymers shown by Formulas (VIII), (IX) or (X).

[0221] As a monomer composition of the copolymer, the percentage of Monomer (A) in the copolymer is preferably 25 to 99 wt% and, more preferably, 40 to 85 wt%. In the case where the percentage of Monomer (A) is too small, water-repellency and resistance to washing may be low and improvement effect of makeup retention may not be exhibited sufficiently, since the part for cross-linking reaction is few. On the other hand, water-repellency and resistance to washing and improvement effect of makeup retention tends to be lowered even in the case where the percentage of Monomer (A) is 100 wt%. Also, flaking is easy to occur. This can be considered that cross-linking reaction is not progressed neatly and a large amount of the unreacted part is remained on the copolymer because cross-linking reaction part is too much to be close.

10 [0222] Monomer (B) adjusts the ratio of Monomer (A). Also, it contributes to water-repellency and inhibits flaking. The percentage of Monomer (B) is 1 wt% or more and, preferably 10 wt% or more in the copolymer. The percentages of other monomers are decreased and the copolymer becomes to have poor solubility against alcohol type solvent in the case where Monomer (B) is too much. Therefore, the percentage of Monomer (B) in the copolymer is 75 wt% or less and, preferably, 60 wt% or less.

20 [0223] Monomer (C) has a siloxane part. Accordingly, Monomer (C) can improve water-repellency and resistance to washing of the cross-linked coat and make feeling of use smooth and favorable. Also, Monomer (C) can inhibit flaking. The percentage of Monomer (C) is 1 wt% or more and, preferably, 5 wt% or more in the copolymer of the present invention. However, when the percentage of Monomer (C) is too large, the percentages of the other monomers become relatively low and resistance to washing tends to be poor. Therefore, the percentage of Monomer (C) in the copolymer is 25 70 wt% or less and, preferably, 60 wt% or less.

[0224] Also, when the copolymer containing Monomer (D) as a constitutive monomer is treated, good texture and moist feeling of use can be given to hair. However, when the percentage of Monomer (D) is too large, water-repellence, resistance to washing and the like become to be poor because hydrophilic nature of the coat becomes high due to amine portion contained in Monomer (D). The percentage of Monomer (D) is 1 to 100 wt% and, preferably, 5 to 50 wt% with respect to a whole amount of Monomers (A) to (C).

30 [0225] Although a compounding amount of the copolymer is not restricted in particular, it is preferably 0.1 to 10 wt% and, more preferably, 1 to 5 wt%. In the case where the compounding amount is too less, the sufficient effect can not be obtained at one time treatment. On the contrary, applicability, spreadability and the like become poor and flaking may occur in the case where the compounding amount is too much.

35 [0226] The pigment and acidic dye, which are comprised into the cosmetic of the present invention is not restricted in particular as long as those are generally compounded into cosmetics.

[0227] As for the acidic dye, in specific, a legal color which is noticed on "Ministrial Ordinance to Determine Tar Color which is Usable for Medicaments and the like" and allowed to use for coloring medicaments, quasi-drugs and cosmetics and which is not shown harmful effect to the human body, can be used. For example, Red No. 3 (erythrosine), Red No. 102 (new coccin), Red No. 106 (acid red), Red No. 201 (lithol rubine B), Red No. 227 (fast acid magenta), Red No. 230 (1) (erythrosine YS), Red No. 203 (2) (erythrosine YSK), Red No. 231 (phloxine BK), Red No. 232 (rose bengal K), Red No. 401 (violamine R), Red No. 502 (ponceau 3R), Red No. 503 (ponceau R), Red No. 504 (ponceau SX), Red No. 506 (fast red S), Yellow No. 202 (2) (uranine K), Yellow No. 4 (tartrazine), Yellow No. 402 (polar yellow 5G), Yellow No. 403 (1) (naphthol yellow S), Yellow No. 406 (metanil yellow), Green No. 3 (fast green FCF), Green No. 201 (alizerine cyanine green F), Green No. 204 (pyranine conc), Green No. 205 (light green SF yellowish), Green No. 401 (naphthol green B), Green No. 402 (guinea green B), Blue No. 1 (brilliant blue FCF), Blue No. 2 (indigo carmine), Blue No. 202 (patent blue NA), Blue No. 205 (alfazurine FG), Brown No. 201 (resorcine brown), Purple No. 401 (alizerol purple), Black No. 401 (naphthol blue black), and the like can be used.

[0228] Pigments used in the present invention include an organic, inorganic and lake pigments.

50 [0229] Example of an organic pigment include, in addition to azo pigment, indigo pigment and phthalocyanine pigment, an organic dye such as β -carotene, carthamin or cochineal.

[0230] Example of an inorganic pigment include, in addition to a coloring pigment such as red iron oxide, yellow iron oxide, black iron oxide, chromium oxide, ultramarine, iron blue and carbon black, an extender pigment such as mica, talc or kaolin, a white pigment such as titanium dioxide or zinc oxide, a pearl pigment such as titanium mica or fish scale flake and a specific functional pigment such as boron nitride, a photochromic pigment, synthetic mica or hybrid fine powder.

55 [0231] Example of a lake pigment include, in addition to a lake pigment such as Red Nos. 202, 204, 206, 207 or 220, a dye lake pigment such as aluminium lake.

[0232] Although a compounding amount of the copolymer in the cosmetic in accordance with the present invention is not restricted in particular, it is preferably 0.1 to 10 wt% and, more preferably, 1 to 5 wt%. In the case where the compounding amount is too less, the sufficient effect can not be obtained at one time treatment. On the contrary, applicability, spreadability and the like become poor and flaking may occur in the case where the compounding amount is too much.

[0233] A compounding amount of the pigment and acidic dye can be properly determined according to the required colorability and is not restricted in particular. However, the compounding amount is usually 0.01 to 20 wt% and, preferably, 0.1 to 10 wt%. Secondary adhesion is easy to occur in the case where the pigment or dye is too much.

[0234] A cosmetic preparation in accordance with the present invention can be, for example, in addition to a hair color such as color spray, color crayon or color mousse, a makeup cosmetic such as nail enamel, mascara or eye brow.

[0235] The present inventors further studied about the effects in the case where the other film-forming ingredients were used in the cosmetic which was comprised the copolymer and pigment and/or acidic dye. As for a film-forming ingredient, siliconized pullulan (substitution degree 1.7, molecular weight of pullulan as a starting material about 200,000) was used.

Example 3-4

Prescription 3-3 (Temporary hair color):

[0236]

Copolymer	5 wt%
Siliconized pullulan	1
Carbon black	1
Ethanol	22.8
Light isoparaffin	70
Silicone rubber	0.2
Perfume	q.s.
Antiseptic	q.s.

[0237] A temporary hair color was prepared according to the above-mentioned prescription 3-3. Also, a hair color, which comprised ethanol instead of siliconized pullulan, was prepared as a control. The test had been conducted in the following method by using each hair color as a sample.

(Coloring retention)

[0238] Each sample was applied to white hair and the hair was left for 3 minutes. Then the hair was washed with water and dried naturally. Thereafter, the hair was washed with a commercially available shampoo and was dried naturally every day, and coloring retention after 10 days was evaluated by visual inspection. Evaluation standard is as follows.

- ⊙ : Very good as compared with the control.
- : Equal to or slightly good as compared with the control.
- △ : Slightly inferior as compared with the control.
- X : Inferior as compared with the control.

(Smoothness)

[0239] Smoothness at 1st and 10th days of the above-mentioned coloring retention test was evaluated by touch. Evaluation standard is as follows.

- ⊙ : Very good as compared with the control.
- : Equal to or slightly good as compared with the control.

Δ : Slightly inferior as compared with the control.

X : Inferior as compared with the control.

(Flaking on repeated application)

[0240] Flaking was evaluated in the same way as the method of the above-mentioned Test Example 1-4.

TABLE 22

Copolymer	Monomer (wt%)				Coloring Retention	Smoothness		Flaking on Repeated Application
	A2	B1	C*	D1		1st	10th	
3-19	60	35	5(C3)	20	⊙	⊙	⊙	⊙
3-20	50	40	10(C1)	-	○	⊙	⊙	⊙
3-21	50	25	25(C2)	-	○	⊙	⊙	⊙
3-22	67	37	-	-	○	⊙	⊙	⊙
3-23	50	-	50(C3)	-	○	⊙	⊙	⊙

[0241] As is clear from TABLE 22, in the case where siliconized pullulan was used together with the copolymer, the effect of coloring retention can be made equal to or better than the case where only the copolymer was used. Touch also can be made more smooth as compared with the case of using the copolymer only, and in particular, the effect with respect to the damaged hair is remarkable. These effects were maintained even when shampoo was repeated. Further, though flaking on repeated application may occur in the case where only the copolymer was used, it can be inhibited by using siliconized pullulan together with. Such effects were the same for the acidic hair color.

TABLE 23

Ingredient	Amount							
	5	5	5	2	2	1	0.1	-
Copolymer 3-19	-	0.1	0.5	0.5	2	5	5	5
Siliconized pullulan	-	○	⊙	⊙	⊙	○	Δ	Δ
Coloring Retention	-	○	⊙	⊙	⊙	○	Δ	Δ
Smoothness	-	○	⊙	⊙	⊙	○	Δ	Δ
1st day	-	○	⊙	⊙	⊙	○	Δ	Δ
10th day	-	○	⊙	⊙	⊙	○	Δ	Δ
Flaking on Repeated Application	Δ	⊙	⊙	⊙	⊙	⊙	⊙	⊙

[0242] TABLE 23 shows the result that the test was conducted in the same way as Test Example 3-4 with changing the ratio of the copolymer and siliconized pullulan. The changing amount of the copolymer and pullulan was adjusted with ethanol.

[0243] Coloring retention tends to be lowered in the case where the copolymer is not much. On the other hand, coloring retention and smoothness are not sufficiently improved and flaking on repeated application may occur in the case where siliconized pullulan is not much. Accordingly, the ratio between the copolymer and siliconized pullulan is preferably 100 : 1 and, more preferably, 50 : 1-1 : 1 by weight.

[0244] As described in the above, by using the copolymer containing reactive silyl groups and the siliconized polysaccharide together with the pigment and/or acidic dye, the cosmetic that coloring retention and feel of use are extremely favorable and flaking on repeated application is not much, can be obtained.

[0245] In the case where only the siliconized polysaccharide was used, coloring retention effect were low as compared with the case where only the copolymer was used. Therefore, it can be considered that these effects are improved by using the siliconized polysaccharide together with the copolymer because at the time of forming the cross-

linked coat the siliconized polysaccharide is included into the coat and the cross-linked coat and the siliconized polysaccharide are synergistically contributed.

Examples 3-1 to 3-3 Color Spray

[0246] The test had been conducted in the same manner as the above-mentioned Test Example 3-1 by using the color sprays of TABLE 24. Every example had high resistance to washing to be excellent in coloring retention as compared with Comparative Example 3-1.

TABLE 24

Ingredient	Example 3-1	Example 3-2	Example 3-3	Comp. Ex. 3-1
(1) Copolymer 3-4	1	3	5	-
(2) Polyvinylpyrrolidone/vinyl acetate copolymer	-	-	-	5
(3) Black iron oxide	1	1	1	1
(4) Ethanol	46	44	42	42
(5) POE (40) hydrogenated castor oil	1	1	1	1
(6) Octyl palmitate	1	1	1	1
(7) LPG (3.5kg/cm ² at 20°C)	50	50	50	50
(8) Perfume	q.s.	q.s.	q.s.	q.s.
Coloring retention	○	⊙	⊙	X

(Manufacturing Process)

[0247] The ingredients (1) to (6) and (8) were stirred and mixed uniformly. Then the mixture and the ingredient (7) were filled into an aerosol container, successively to obtain a color spray.

Examples 3-4 to 3-6 Hair Mist

[0248] The test had been conducted in the same manner as the above-mentioned Test Example 3-1 by using the hair mists of TABLE 25. Every example had high resistance to washing to be excellent in coloring retention as compared with Comparative Example 3-2.

TABLE 25

Ingredient	Example 3-4	Example 3-5	Example 3-6	Comp. Ex. 3-2
(1) Copolymer 3-1	1	3	5	-
(2) Polyvinylalcohol/<-> vinyl acetate copolymer	-	-	-	5
(3) Carbon black	1	1	1	1
(4) Ethanol	96	94	92	92
(5) POE (9) laurylether	1	1	1	1
(6) Dimethylpolysiloxane (5cps)	1	1	1	1
(7) Perfume	q.s.	q.s.	q.s.	q.s.
Coloring retention	○	○	⊙	X

(Manufacturing Process)

[0249] The ingredients (1) to (7) were stirred and mixed uniformly. The mixture was filled into a container, thereby obtaining a hair mist.

Examples 3-7 to 3-9 Color Spray

[0250] The test had been conducted in the same manner as the above-mentioned Test Example 3-1 by using the color sprays of TABLE 26. Every example had high resistance to washing to be excellent in coloring retention as compared with Comparative Example 3-3.

TABLE 26

Ingredient	Example 3-7	Example 3-8	Example 3-9	Comp. Ex. 3-3
(1) Copolymer 3-5	1	3	5	-
(2) Polyvinylpyrrolidone/vinyl acetate copolymer	-	-	-	5
(3) Resorcline brown	1	1	1	1
(4) Ethanol	48.2	46.2	44.2	49.2
(5) Benzyl alcohol	5	5	5	5
(6) Citric acid	0.3	0.3	0.3	0.3
(7) POE (100) hydrogenated castor oil	1	1	1	1
(8) Highly polymerized dimethylpolysiloxane	0.5	0.5	0.5	0.5
(9) Dimethyl polysiloxane (5cps)	3	3	3	3
(10) LPG (3.5kg/cm ² at 20°C)	40	40	40	40
(11) Perfume	q.s.	q.s.	q.s.	q.s.
Coloring retention	⊙	⊙	⊙	Δ

(Manufacturing Process)

[0251] The ingredients (1) to (9) and (11) were stirred and mixed uniformly. Then the mixture and the ingredient (10) were filled into an aerosol container, successively to obtain a color spray.

Example 3-10 Nail Enamel

[0252] Nail enamels were prepared according to the following prescription 3-4 by using the foregoing Copolymers 3-1 to 3-6. The prepared nail enamel was applied on the nails of female panel. After drying, the nails were washed with water. Thereafter, the nails were observed in every day. A crack or peeling was observed within 3 days in the case where ethanol was comprised instead of the copolymer. However, crack or peeling was absolutely not observed for 7 days or more and coloring retention was maintained in the case where the copolymer was comprised.

Prescription 3-4:

[0253]

Nitrocellulose	10 wt%
Alkyd resin	10

(continued)

Acetyltributyl citrate	5
Ethyl acetate	10
Butyl acetate	5
Copolymer	5
Ethanol	55
Rhodamine B	q.s.
Suspending agent	q.s.

(Manufacturing Process)

[0254] Rhodamine B was added to a part of alkyd resin and a part of acetyltributyl citrate and the mixture was sufficiently kneaded. The other ingredients were mixed and dissolved and the former mixture was added thereto. The mixture was dispersed in uniform to obtain a nail enamel.

Example 3-11 Mascara

[0255] Mascaras were prepared according to the following prescription 3-5 by using the above-mentioned Copolymers 3-1 to 3-6. Each of mascara was applied on the eyelashes and was washed with water after drying. Thereafter, eyelashes were washed with a commercially available detergent and dried repeatedly.

[0256] As a result, as shown in TABLE 27, crocking of color was clearly prevented and coloring retention was improved by using the copolymer.

Prescription 3-5:

Black iron oxide	10 wt%
Solid paraffin	5
Lanolin wax	5
Light isoparaffin	5
Ethanol	70
Copolymer	5
Perfume	q.s.

(Manufacturing Process)

[0258] Each ingredient was mixed successively and dispersed in uniform to obtain a mascara.

TABLE 27

Copolymer	Coloring Retention*
Copolymer 3-1	○
Copolymer 3-2	⊙
Copolymer 3-3	⊙
Copolymer 3-4	⊙
Copolymer 3-5	⊙
Copolymer 3-6	⊙
Nothing (control)	X

* Evaluation standard of coloring retention:

⊙ . . . Color was crocked by washing 5 times or more.

○ . . . Color was crocked by washing 3 times or more.

X . . . Color was crocked by washing once.

Examples 3-12 to 3-14 Color Spray

[0259] The test had been conducted in the same manner as the above-mentioned Test Example 3-1 by using the color sprays of TABLE 28. Every example had high resistance to washing to be excellent in coloring retention as compared with Comparative Example 3-4. Also, feeling of use thereof was smooth.

TABLE 28

Ingredient	Example 3-12	Example 3-13	Example 3-14	Comp. Ex. 3-4
(1) Copolymer 3-9	1	-	-	-
(2) Copolymer 3-11	-	1	-	-
(3) Copolymer 3-12	-	-	1	-
(4) Polyvinylpyrrolidone/vinyl acetate copolymer	-	-	-	1
(5) Black iron oxide	1	1	1	1
(6) Ethanol	46	46	46	46
(7) POE (40) hydrogenated castor oil	1	1	1	1
(8) Octyl palmitate	1	1	1	1
(9) LPG (3.5kg/m ² at 20°C)	50	50	50	50
(10) Perfume	q.s.	q.s.	q.s.	q.s.
Coloring Retention	⊙	⊙	⊙	X
Smoothness	⊙	⊙	⊙	X

(Manufacturing process)

[0260] The ingredients (1) to (8) and (10) were stirred and mixed uniformly. Then the mixture and the ingredient (9) were filled into an aerosol container, successively, to obtain a color spray.

Examples 3-15 to 3-17 Hair Mist

[0261] The test had been conducted in the same manner as the above-mentioned Test Example 3-1 by using the hair mists of TABLE 29. Every example had high resistance to washing to be excellent in coloring retention as compared

with Comparative Example 3-5. Also, feeling of use thereof was smooth.

TABLE 29

Ingredient	Example 3-15	Example 3-16	Example 3-17	Comp. Ex. 3-5
(1) Copolymer 3-8	1	-	-	-
(2) Copolymer 3-9	-	1	-	-
(3) Copolymer 3-13	-	-	1	-
(4) Polyvinylalcohol vinyl acetate copolymer	-	-	-	5
(5) Carbon black	1	1	1	1
(6) Ethanol	96	96	96	96
(7) POE (9) laurylether	1	1	1	1
(8) Dimethylpolysiloxane (5cps)	1	1	1	1
(9) Perfume	q.s.	q.s.	q.s.	q.s.
Coloring Retention	⊙	⊙	⊙	X
Smoothness	⊙	⊙	⊙	X

(Manufacturing process)

[0262] The ingredients (1) to (9) were stirred and mixed in uniform. The mixture was filled into a container, thereby obtaining a hair mist.

Examples 3-18 to 3-20 Color Spray

[0263] The test had been conducted in the same manner as the above-mentioned Test Example 3-1 by using the color sprays of TABLE 30. Every example had high resistance to washing to be excellent in coloring retention as compared with Comparative Example 3-6.

TABLE 30

Ingredient	Example 3-18	Example 3-19	Example 3-20	Comp. Ex. 3-6
(1) Copolymer 3-11	1	-	-	-
(2) Copolymer 3-13	-	1	-	-
(3) Copolymer 3-14	-	-	1	-
(4) Polyvinylpyrrolidone/vinyl acetate copolymer	-	-	-	1
(5) Resorcine brown	1	1	1	1
(6) Ethanol	48.2	48.2	48.2	48.2
(7) Benzyl alcohol	5	5	5	5
(8) Citric acid	0.3	0.3	0.3	0.3
(9) POE (100) hydrogenated castor oil	1	1	1	1
(10) Highly polymerized dimethyl-polysiloxane	0.5	0.5	0.5	0.5
(11) Dimethyl polysiloxane (5cps)	3	3	3	3
(12) LPG (3.5kg/cm ² at 20°C)	40	40	40	40

TABLE 30 (continued)

Ingredient	Example 3-18	Example 3-19	Example 3-20	Comp. Ex. 3-6
(13) Perfume	q.s.	q.s.	q.s.	q.s.
Coloring Retention	⊙	⊙	⊙	X
Smoothness	⊙	⊙	⊙	X

(Manufacturing Process)

[0264] The ingredients (1) to (11) and (13) were stirred and mixed in uniform. Then the mixture and the ingredient (12) were filled into an aerosol container, successively to obtain a color spray.

Example 3-21 Nail Enamel

[0265] Nail enamels were prepared according to the following prescription 3-6 by using the above-mentioned Copolymers 3-11, 12 and 14. The nail enamel was applied on the nails of female panel. After drying, the nail was washed with water. Thereafter, the nail was observed in every day. Crack or peeling was observed within 3 days in the case where ethanol was comprised instead of the copolymer. However, crack or peeling of control was absolutely not observed for 10 days or more and coloring retention was maintained in the case where the copolymer was comprised.

Prescription 3-6:

[0266]

Nitrocellulose	10 wt%
Alkyd resin	10
Acetyltriethyl citrate	5
Ethyl acetate	10
Butyl acetate	5
Copolymer	5
Ethanol	55
Rhodamine B	q.s.
Suspending agent	q.s.

(Manufacturing process)

[0267] Rhodamine B was added to a part of alkyd resin and a part of acetyl triethyl citrate and the mixture was fully kneaded. The other ingredients were mixed and dissolved, and the former mixture was added thereto. The mixture was dispersed in uniform to obtain a nail enamel.

Example 3-22

[0268] The copolymers 3-24 to 3-26 were synthesized according to the following method tested in the same way as the above mentioned Test Example 3-1. As a result, every copolymer had high coloring retention effect and favorable feeling of use as shown in TABLE 31. Also, flaking was not observed in every copolymer.

Copolymer 3-24

[0269] 12.0g of Monomer A2 and 6.0g of Monomer B1 were dissolved into 100ml of ethanol and the solution was stirred with heating under nitrogen gas stream for 1 hour at 70°C. 0.05g of dimethyl 2,2'-azobis(isobutyrate) was added

to the solution and the mixture was reacted over night. The reaction mixture was cooled down to room temperature and concentrated under a vacuum. The residue was dissolved into 10ml of ethanol and the solution was added to 500ml of n-hexane. The deposits were collected to obtain the aimed copolymer.

5 Copolymer 3-25

[0270] In the similar manner to Copolymer 3-24, except for using 10.0g of Monomer A2, 2.0g of Monomer B1, and 1.0g of Monomer D1, the aimed copolymer was obtained.

10 Copolymer 3-26

[0271] In the similar manner to Copolymer 3-24, except for using 10.0g of Monomer A2, 10.0g of Monomer C4, and 0.5g of Monomer D1, the aimed copolymer was obtained.

TABLE 31

Acidic hair color (prescription 3-2, Copolymer 2 wt%)							
Copolymer	Monomer(wt%)				Coloring Retention	Smoothness	Texture
	A2	B1	C4	D1			
3-24	67	-	-	33	○	○	◎
3-25	77	15	-	8	◎	○	◎
3-26	49	-	49	2	◎	◎	◎

Example 3-23 Color Spray

[0272]

Red iron oxide	1 wt%
Copolymer 3-19	4
Siliconized pullulan	1
Silicone rubber	0.2
Light isoparaffin	70
Ethanol	23.8
Perfume	q.s.
Antiseptic	q.s.

(Manufacturing Process)

[0273] After silicone rubber and siliconized pullulan were dissolved into light isoparaffin, a stock solution of a spray was prepared by adding the ethanol solution of Copolymer 3-19 and the other ingredients to the former solution. 70 parts of the stocked solution was filled into a can and a valve was mounted. 30 parts of dimethyl ether gas was filled into the can to obtain a color spray.

[0274] The color spray had favorable coloring retention and feeling of use and inhibited flaking on repeated application as compared with the color spray that siliconized pullulan was not comprised.

Example 3-24 Nail Enamel

[0275]

Pigment	2 wt%
Copolymer 3-22	7
Siliconized pullulan	0.5
Light isoparaffin	45
Ethanol	45.5
Perfume	q.s.
Antiseptic	q.s.

(Manufacturing Process)

[0276] After siliconized pullulan was dissolved into light isoparaffin, the ethanol solution of Copolymer 3-22 and the other ingredients were added to the former solution, thereby obtaining a nail enamel.

[0277] The nail enamel had favorable coloring retention and feeling of use and inhibited flaking on repeated application as compared with the nail enamel that siliconized pullulan was not comprised.

Example 3-25 Oily Water-Proof Mascara

[0278]

Iron oxide	10 wt%
Copolymer 3-20	2
Siliconized pullulan	2
Light isoparaffin	50
Ethanol	20
Solid paraffin	5
Lanolin wax	5
Glycerine	6
Perfume	q.s.
Antioxidant	q.s.

(Manufacturing Process)

[0279] After siliconized pullulan, solid paraffin and lanolin wax were dissolved into light isoparaffin, the ethanol solution of Copolymer 3-20 and the glycerine dispersion of iron oxide was added to the former mixture to obtain a mascara.

[0280] The mascara had favorable coloring retention and feeling of use and inhibited flaking on repeated application as compared with the mascara that siliconized pullulan was not comprised.

(Cosmetic Packs)

[0281] Presently, various packs (masks) which express removal action to wastes of sebum, old horny layer, dirt or the like have been developed in the field of cosmetics.

[0282] Such cosmetic pack is classified broadly into: a peel-off type which is a paste or jelly and used by peeling off a coat formed after applying and drying; a type which is removed with wiping or washdown after applying; a type that a pack composition is adhered to a sheet such as nonwoven fabric sheet and the sheet is peeled off after patching; or the like. A cosmetic pack, which mainly aims skin cleaning action is almost the peel-off type or patching type.

5 [0283] In these cosmetic packs, in addition to skin-cleaning action, strippability that a pack coat is peeled off completely without remaining on the skin, is required. Also, in the peel-off type pack, facility for stretching the cosmetic pack on the skin and coat strength are also important.

[0284] However, the pack, which sufficiently satisfy the consumer in this respect had not been obtained yet. Namely, in the cosmetic packs of peel-off type or patching type, there is a limit of its adhesiveness to the skin and removal activity to wastes of sebum or old horny layer, because they have necessity to be peeled off in later.

10 [0285] Therefore, the present inventors studied about the effects in the case where the copolymer containing reactive silyl groups was comprised into such peel-off type cosmetic pack.

Test Example 4-1

15 i) Synthesis of Copolymer

Copolymer 4-1

20 [0286] 12.0g of 3-methacryloxypropyltrimethoxysilane (Monomer A1) and 8.0g of methyl methacrylate (Monomer B1) were dissolved into 100ml of ethanol and the solution was stirred with heating under nitrogen gas stream for 1 hour at 70°C. 0.05g of potassium persulfate was added to the solution and the mixture was reacted over night. The reaction mixture was cooled down to room temperature and concentrated under a vacuum. The residue was dissolved into 10ml of ethanol and the mixture was added to 500ml of n-hexane. The deposits were collected to obtain the aimed copolymer.

25 [0287] In the NMR spectral data (solvent CDCl_3 or DMSO-d_6) of the resulting copolymer, a peak of hydrogen atom of $\text{CH}_2=\text{C}$ derived from the monomers used as starting materials that the peak should be observed in 6-7 ppm or near, was not observed. As a result, generation of copolymer was confirmed. Also, in the present invention, generation of the other copolymers were confirmed in the similar manner.

30 Copolymer 4-2

[0288] In the similar manner to the synthesis of Copolymer 1, except for using 10.0g of Monomer A1, 2.0g of Monomer B1 and 8.0g of 3-methacryloxypropyl(trimethylsiloxy) silane (Monomer C3), the aimed copolymer was obtained.

35 Copolymer 4-3

[0289] In the similar manner to the synthesis of Copolymer 1, except for using 12.0g of Monomer A1, 5.0g of Monomer B1 and 3.0g of 3-methacryloxypropyldimethyl-polysiloxane (Monomer C1), the aimed copolymer was obtained.

40 Copolymer 4-4

[0290] In the similar manner to the synthesis of Copolymer 1, except for using 12.0g of Monomer A1, 7.0g of Monomer B1 and 1.0g of Monomer C2, the aimed copolymer was obtained.

45 ii) Preparation of Sample

Oil phase (first agent):

50 [0291]

Polyvinyl acetate	15 wt%
Polyvinyl alcohol	10
Sorbitol	5

55

(continued)

PEG 400	5
Liquid isoparaffin	2
Squalane	2
POE sorbitan monostearate	1
Ethanol	10
Copolymer	10
Water phase (second agent):	
Titanium dioxide	5
Talc	10
Purified water	25

(Manufacturing Process)

[0292] The first and second agents were prepared by sufficiently mixing components of oil phase and water phase separately. A control wherein the copolymer was not comprised (wherein, 35 wt% of purified water was used) was also prepared.

iii) Test Method

[0293] The first and second agents were mixed just before the test. The mixture was applied on the face. After drying naturally, the pack preparation was peeled off 20 of professional panel evaluated with feelings with respect to applicability, strippability, coat strength and skin-cleaning effect at this time. Evaluation standard was as follows.

- ◎ : 15 or more answered favorable.
 ○ : 10 to 14 answered favorable.
 △ : 5 to 9 answered favorable.
 X : 4 or less answered favorable.

TABLE 32

Copolymer (constitutive monomer)	Applicability	Strippability	Coat Strength	Cleaning Effect
No copolymer (control)	△	△	△	△
Copolymer 4-1 (A1-B1)	△	○	◎	◎
Copolymer 4-2 (A1-B1-C3)	◎	◎	◎	◎
Copolymer 4-3 (A1-B1-C1)	○	◎	◎	◎
Copolymer 4-4 (A1-B1-C2)	○	◎	◎	◎

[0294] As is clear from TABLE 32, the cosmetic pack comprising any of Copolymers 1 to 4 having Monomers (A) and (B) as a constitutive monomer had extremely high coat strength and skin-cleaning effect and was excellent in strippability, as compared with the case that these copolymers were not comprised. In particular, applicability and strippability can be further improved without loss of coat strength and skin-cleaning effect, in the case where the copolymer having Monomers (A) to (C) was comprised. Also, a coat of the pack became flexible to be improved its fitness feeling when the copolymer has Monomer (C).

TABLE 33

Monomer composition of copolymer (A1)/(B1) (wt%)	Coat Strength	Cleaning Effect
10/90	Δ	Δ
25/75	○	○
40/60	⊙	⊙
60/40	⊙	⊙
85/15	⊙	⊙
96/4	○	○
100/0	Δ	Δ

[0295] TABLE 33 shows the result when the test was conducted in the same way as the above-mentioned Test Example 4-1 with a change of the monomer composition of the copolymer.

[0296] As is clear from TABLE 33, the cosmetic pack comprising Copolymer consist of Monomers (A) and (B) can form a strong pack coat on skin to exhibit high skin-cleaning effect. However, these effects are not sufficient when the percentage of Monomer (A) in the copolymer is too small or too large. Accordingly, it is understood that the percentage of Monomer (A) in the copolymer is 25 to 99 wt% and, preferably, 40 to 85 wt%.

TABLE 34

Monomer Composition of Copolymer (A1)/(B1)/(C3) (wt%)	Applicability	Strippability	Cleaning Effect
60/40/0	Δ	○	⊙
60/35/5	○	⊙	⊙
60/25/15	⊙	⊙	⊙
50/10/40	⊙	⊙	⊙

[0297] As is clear from TABLE 34, usability such as applicability or strippability can be improved without a loss of skin-cleaning effect by introducing Monomer (C) into the Copolymer consist of Monomers (A) and (B). For such effects, the percentage of Monomer (C) in the copolymer is 1 wt% or more and, preferably, 5 wt% or more.

TABLE 35

Amount of Copolymer	Applicability	Strippability	Coat Strength	Cleaning Effect
1 wt%	Δ	Δ	Δ	Δ
5	○	○	○	○
10	⊙	⊙	⊙	⊙
20	⊙	⊙	⊙	⊙
50	⊙	⊙	⊙	⊙

[0298] TABLE 35 shows the result in the case where the amount of the copolymer is changed in the cosmetic pack comprising the Copolymer 4-2. The amount of change caused by increase and decrease of the copolymer was adjusted with purified water.

[0299] As is clear from TABLE 35, skin-cleaning effect is not exhibited sufficiently and applicability, strippability and coat strength are also deteriorated in the case where the amount of the copolymer in the cosmetic pack is too less. On the contrary, applicability or strippability tends to be lowered in the case where the amount is too much. Therefore, the

amount of the copolymer in the cosmetic pack is 5 to 50 wt% and, preferably, 10 to 20 wt%.

[0300] As mentioned above, when the copolymer containing reactive silyl groups is comprised into the cosmetic pack, and a coat formed by cross-linking with hydrolyzing the copolymer on the skin is peeled off from the skin after drying, the effect that wastes of sebum, old horny layer and dirt of the skin are completely removed with the pack coat and feeling of use is favorable, can be worked. Also, this pack coat is hard to be torn on peeling, and can be peeled off completely.

[0301] It is considered that such effect can be obtained because due to hydrolyzing after applying the cosmetic pack comprising the copolymer, the cross-linked copolymer is strongly and uniformly coated on surface of the skin in network state by cross-linking on the applied portion to form the strong pack coat.

10 [0302] A preferred example of the copolymer to be comprised to the cosmetic pack in the present invention, the copolymer shown by Formula (IX) can be mentioned above.

[0303] As a monomer composition of the copolymer, the percentage of Monomer (A) in the copolymer is preferably 25 to 99 wt% and, more preferably, 40 to 85 wt%. In the case where the percentage of Monomer (A) is too small, skin-cleaning effect is not exhibited sufficiently, since the part for cross-linking reaction is few. On the other hand, skin-cleaning effect tends to be deteriorated in the case where the percentage of Monomer (A) is too large. It can be considered that this is a result that cross-linking reaction is not progressed neatly and a large amount of the unreacted part is remained on the cross-linked copolymer because the part for cross-linking reaction is too much to be close. Also, flexibility of the cross-linked coat may be deteriorated to be inferior in usability.

[0304] Monomer (B) adjusts the ratio of Monomer (A). Also, since the copolymer consists of Monomers (A) and (C) has too stickiness to be difficult to use, Monomer (B) can inhibit such stickiness and adjust the nature of the coat. The percentage of Monomer (B) is preferably 1 wt% or more and, more preferably, 15 wt% or more in the copolymer. In the case where the percentage of Monomer (B) is too large, the percentages of the other monomers are decreased and the copolymer becomes to have poor solubility against alcohol type solvents. Therefore, the percentage of Monomer (B) is preferably 75 wt% or less and, more preferably, 60 wt% or less.

25 [0305] Monomer (C) has a siloxane part and gives the coat plasticity. Also, Monomer (C) contributes to applicability, flexibility of the coat, strippability or the like. The percentage of Monomer (C) is preferably 1 wt% or more and, more preferably, 5 wt% or more in the copolymer of the present invention. However, when the percentage of Monomer (C) is too large, the percentages of the other monomers become relatively small and skin-cleaning effect tends to be deteriorated. Therefore, the percentage of Monomer (C) is 74 wt% or less and, preferably, 60 wt% or less.

30 [0306] In the cosmetic pack of the present invention, a concentration of the copolymer is not restricted in particular. However, a concentration of the copolymer in the final composition is preferably 5 to 50 wt% and, more preferably, 10 to 20 wt%. In the case where the amount is too little, the sufficient effect can not be obtained. On the contrary, applicability, feeling of use and the like may become inferior in the case where the amount is too much.

[0307] A method for pack in accordance with the present invention is characterized in that the cosmetic pack in accordance with the present invention is hydrolyzed on the skin to cross-link molecules of the copolymer and then the pack coat formed is peeled off after drying. As a method for drying, natural drying may be usually available. Though a method for cross-linking is described in the foregoing, it is preferable that the copolymer is mixed with water, acid or alkali and the mixture is immediately applied, in view of strippability.

35 [0308] A preferred example of the cosmetic pack of the present invention can be a cosmetic pack consisting of plural agents. Examples of such cosmetic pack include a two-agents type cosmetic pack consisting of the first agent which is a non-aqueous composition containing the copolymer and the second agent which is an aqueous composition containing water. A method for treating the cosmetic pack, it is preferable to mix the first and the second agents in advance immediately before application and to peel off the pack after applying and drying. Strippability is favorable in the case where such two-agents type cosmetic pack is used. Needless to say, it is possible to mix an optional composition excluding the first and second agents in the present invention. Also, a final mixture of such the plural-agents type cosmetic pack is within the category of the present invention.

[0309] The type of the cosmetic pack of the present invention is called as peel-off type or patching type which is peeled off after applying. The preparation form can be various formulations such as solubilization type, dispersion type or emulsion type. A property of the cosmetic pack can be made liquid, paste, jelly, gel or the like. Also, a sheet type pack can be made by applying the cosmetic pack on the sheet of nonwoven fabric or the like.

50 [0310] The other ingredients that are generally comprised into cosmetic packs or the other cosmetics, can be comprised into the cosmetic pack of the present invention as long as the effect of the present invention is not spoiled. For example, in addition to surfactants, pH adjustors, antiseptics, antioxidants, chelating agents, thickening agents, film-forming ingredients, oily components, highly polymerized compounds, humectants, powders, coloring matters and the like, drugs such as whitening agents or germicidal agents can be used.

55 [0311] In particular, plasticity or strippability of the coat can be improved by an oily component, silicone rubber or the other polymers, or clay mineral. Also, strippability can be improved by the powder.

(Application for Other Materials To Be Treated)

[0312] The copolymer of the present invention has an excellent coat-forming property and resistance to washing. Accordingly, the present inventors studied about the effect with respect to the material except for the hair or skin, e.g.,
5 fiber, paper, glass and the like.

Test Example 5-1

[0313] First, the test was conducted according to the following method so as to investigate the effect to fiber.
10 (Water-repellency)

[0314] 5% ethanol solution of each copolymer was sprayed on a cotton shirt and the shirt was dried naturally. A few drops of water were dropped onto the shirt and its water-repellency was evaluated with visual sensation. Also, a set of
15 washing the shirt with a washing machine by using a commercially available household detergent and drying naturally was repeated 10 times. Thereafter, water-repellency was evaluated in the same way as mentioned above.

Evaluation standard

20 [0315]

- ⊙ : Extremely favorable
- : Favorable
- △ : Slightly unfavorable
- 25 X : Unfavorable

(Smoothness)

[0316] 2g of 5% ethanol solution of each copolymer was applied on 10g of a sheet of cotton fabric and dried naturally.
30 Smoothness of this fabric had been evaluated by 20 of professional panel with touch.

Evaluation standard

35 [0317]

- ⊙ : 15 or more answered favorable.
- : 10 to 14 answered favorable.
- △ : 5 to 9 answered favorable.
- 40 X : 4 or less answered favorable.

(Suitability for sizing)

[0318] 5% ethanol solution of the tested copolymer was sprayed on a cotton shirt and was hardened by ironing with a steam iron. The state of shirt immediately after ironing has been evaluated with touch. Further, suitability for 10 times
45 of sizing after washing and drying in the similar manner to the water-repellency test mentioned above.

Evaluation standard

50 [0319]

- ⊙ : Extremely favorable.
- : Favorable.
- △ : Slightly unfavorable.
- 55 X : Unfavorable.

(Crease-smoothing property/crease resistance)

[0320] In the similar manner to the above-mentioned suitability for sizing test, the states of crease after ironing and

10 times of washing and drying were judged with visual sensation and thereby crease-smoothing property/crease resistance was evaluated.

Evaluation standard

[0321]

- ⊙ : Extremely favorable.
○ : Favorable.
△ : Slightly unfavorable.
X : Unfavorable.

(Unsusceptibility to fouling)

[0322] A drop of coffee was dropped onto the shirt that was treated in the same way as the above-mentioned water-repellency test. Attachment degree of fouling after wiping the drop with another fabric was judged with visual sensation. Thereby, unsusceptibility to fouling was evaluated.

Evaluation standard

[0323]

- ⊙ : Extremely favorable
○ : Favorable
△ : Slightly unfavorable
X : Unfavorable

(Texture)

[0324] 2g of 5% ethanol solution of each copolymer was applied on 10g of a sheet of cotton fabric and dried naturally. Texture of this fabric had been evaluated by 20 of professional panel with touch.

Evaluation standard

[0325]

- ⊙ : 15 or more answered favorable.
○ : 10 to 14 answered favorable.
△ : 5 to 9 answered favorable.
X : 4 or less answered favorable.

TABLE 36

Copolymer	Monomer (wt%)		Water-repellency		Unsusceptibility to Fouling	Smoothness
	A2	B1	just after treatment	after washing		
5-1	20	80	○	X	○	△
5-2	33	67	○	○	○	△
5-3	50	50	○	○	○	△
5-4	67	33	○	○	○	△
5-5	83	17	○	△	○	△
5-6	100	0	△	X	△	X
Untreated	-	-	X	X	X	X

[0326] As is clear from TABLE 36, the cross-linked coat formed by the copolymer consisting of Monomers (A) and (B) could provide favorable water-repellency and unsusceptibility to fouling. Resistance to washing was not sufficiently obtained to be poor in retention of its effect in the case where Monomer (A) in the copolymer was too less. On the contrary, water-repellency, resistance to washing and unsusceptibility to fouling tends to be deteriorated in the case where Monomer (A) is 100%. In this case, further, feeling of use was inferior and flaking occurred. Accordingly, the percentage of Monomer (A) is preferably 25 to 85 wt% and, more preferably, 40 to 75 wt% in the copolymer.

[0327] Next, the copolymer having Monomers (C) and (D) along with Monomers (A) and (B) was tested.

TABLE 37

Copolymer	Monomer (wt%)			Water-repellency		Unsusceptibility to Fouling	Smoothness
	A2	B1	C2	just after treatment	after washing		
5-7	10	40	50	○	X	○	⊙
5-8	20	40	40	○	X	⊙	⊙
5-9	45	50	5	⊙	⊙	⊙	⊙
5-10	50	25	25	⊙	⊙	⊙	⊙
5-11	50	10	40	⊙	⊙	⊙	⊙
5-12	55.6	33.3	11.1	⊙	⊙	⊙	⊙
5-13	60	35	5	⊙	⊙	⊙	⊙
5-14	71.4	14.3	14.3	⊙	⊙	⊙	⊙
5-15	85	10	5	○	△	○	⊙

[0328] As is clear from TABLES 36 and 37, in the case where the copolymer consisting of Monomers (A) to (C) are treated, water-repellency, resistance to washing and unsusceptibility to fouling can be considerably improved as compared with the copolymer consisting of Monomers (A) and (B). Also, the result of the treated shirts was very smooth to be extremely favorable. In order to obtain such effects, the percentage of Monomer (C) in the copolymer is 1 wt% or more and, preferably, 5 wt% or more.

[0329] Copolymer 5-16 consisting of Monomers (A) and (C) has stickiness. As for Monomer B, it was indicated that a presence of Monomer (B) inhibited stickiness caused by Monomer (C) to give a moderate nature to the coat. The percentage of Monomer (B) in the copolymer is 5 wt% or more and, preferably, 10 wt% or more.

TABLE 38

Copolymer	Monomer (wt%)			Water-repellency		Unsusceptibility to Fouling	Smoothness
	A2	B1	C*	just after treatment	after washing		
5-16	50	10	40(C1)	⊙	⊙	⊙	⊙
5-17	60	35	5(C3)	⊙	⊙	⊙	⊙
5-18	60	35	5(C4)	⊙	⊙	⊙	⊙
5-19	50	25	25(C4)	⊙	○	⊙	⊙

* The inside of () represents Monomer (C) used.

[0330] As is clear from TABLE 38, even when Monomer (C) in the copolymer was Monomer C1, C3 or C4, the same effect could be obtained in the case where Monomer (C) is Monomer C2.

TABLE 39

Copolymer	Monomer (parts by weight)					Water-repellency		Texture
	A1	B1	C3	C4	D1	just after treatment	after washing	
5-17	60	35	5	-	-	⊙	⊙	Δ
5-18	60	35	-	5	-	⊙	⊙	Δ
5-20	60	35	5	-	10	⊙	⊙	⊙
5-21	60	35	-	5	10	⊙	○	⊙
5-22	60	35	-	5	20	⊙	○	⊙
5-23	60	35	-	5	50	○	○	⊙
5-24	60	35	-	5	100	Δ	X	⊙

[0331] As is clear from TABLE 39, the cross-linked coat of the copolymer consisting of Monomers (A) to (D) can give fiber good texture and moisture touch. In the case where Monomer (D) is too much, water-repellency and resistance to washing tend to be deteriorated since hydrophilic property of the cross-linked coat becomes high. Accordingly, the percentage of Monomer (D) is 1 to 100 wt% and, preferably, 5 to 50 wt% with respect to a whole amount of Monomers (A) to (C) in the copolymer.

TABLE 40

	Copolymer					Untreated
	5-10	5-16	5-17	5-19	5-21	
Suitability for Sizing						
(just after treatment)	⊙	⊙	⊙	⊙	⊙	X
(after washing)	⊙	⊙	⊙	○	○	X
Crease-smoothing property/crease resistance						
(just after ironing)	⊙	⊙	⊙	⊙	⊙	X
(after washing)	⊙	○	⊙	○	○	X

[0332] As is clear from TABLE 40, the cross-linked coat of the copolymer in accordance with the present invention exhibits an excellent effect in suitability for sizing and crease-smoothing property/crease resistance with respect to fiber.

TABLE 41

	Copolymer					Untreated
	5-10	5-16	5-17	5-19	5-21	
Water-repellency (just after treatment)	⊙	⊙	⊙	⊙	⊙	X
Unsusceptibility to Fouling	⊙	⊙	⊙	⊙	⊙	X

[0333] TABLE 41 shows the result of water-repellency test and unsusceptibility to fouling test conducted in the same way by using paper instead of a cotton shirt. As a result, it is understood that high water-repellency and unsusceptibility to fouling can be obtained even in the case where the copolymer of the present invention is treated on paper.

TABLE 42

	Copolymer					Untreated
	5-10	5-16	5-17	5-19	5-21	
Angle of contact	96.0	96.4	92.0	97.0	94.6	9.7
Angle of inclination	13.0	11.0	14.2	15.0	13.8	- *

* Impossible to measure because waterdrop was remained.

[0334] TABLE 42 is the result when hydrophobic degree of glass is investigated by using a glass plate in the place of a cotton shirt and by treating in the similar manner to the above-mentioned water-repellency test. Hydrophobic degree was evaluated by the angles of contact and inclination with respect to water. A drop of water was dropped onto a glass and the angle of contact was measured. Also, a glass was gradually inclined and the angle at just when the waterdrop started to move was measured as the angle of inclination. The larger the angle of contact is and the smaller the angle of inclination is, the larger hydrophobic degree can be evaluated.

[0335] As a result, the glass plate treated with the copolymer in accordance with the present invention has very large angle of contact to water as compared with the untreated glass plate. On the other hand, the angle of inclination is too small. Accordingly, it was indicated that the copolymer of the present invention can give the glass plate very high hydrophobic ability.

[0336] As mentioned above, the copolymer of the present invention formed the cross-linked coat which was excellent in water-repellency and unsusceptibility to fouling by cross-linking reaction on the treated material. Also, the coat is very hard to be removed even with water or detergent to these effects exhibit continuously. Accordingly, the copolymer can be used as a water-repellent or a stain proofing agent for various materials. Also, the copolymer of the present invention is preferable as a treatment for fiber such as water-repellent for fiber, size for fiber or crease-resistant agent because the cross-linked coat causes very few flaking and when the copolymer is applied to a treatment for fiber, the cross-linked coat has suitability for sizing, crease-resistance, and very excellent feeling of use.

[0337] A preferable example of the copolymer used for such water-repellent or treatment for fiber can be shown by Formula (IX) or (X).

[0338] As a monomer composition of the copolymer, the percentage of Monomer (A) in the copolymer is preferably 25 to 85 wt% and, more preferably 40 to 75 wt%. In the case where the percentage of Monomer (A) is too small, the effect such as water-repellency or resistance to washing may not be sufficiently exhibited since the part for the cross-linking reaction is few. On the contrary, water-repellency or resistance to washing tends to be deteriorated in the case where the percentage of Monomer (A) is too large. It can be considered that this is the result that cross-linking reaction is not progressed neatly and a large amount of the unreacted part is remained on the cross-linked copolymer because the part for cross-linking reaction is too much to be close. Also, feeling of use may be worse and flaking may be caused.

[0339] Monomer (B) contributes to water-repellency of the cross-linked coat. Also, Monomer (B) inhibits flaking and stickiness caused by Monomer (C) to adjust the nature of the cross-linked coat. The percentage of Monomer (B) is 5 wt% or more and, preferably, 10 wt% or more in the copolymer. The percentages of other monomers are decreased and the copolymer becomes to have poor solubility against alcohol type solvent in the case where the percentage of Monomer (B) is too large. Therefore, the percentage of Monomer (B) is 75 wt% or less and, preferably, 60 wt% or less.

[0340] Monomer (C) has a siloxane part. Accordingly, Monomer (C) can remarkably improve water-repellency of the cross-linked coat and can give fiber smoothness to make the result favorable. Monomer (C) also inhibits flaking. The percentage of Monomer (C) is 1 wt% or more and, preferably, 5 wt% or more in the copolymer of the present invention. However, when the percentage of Monomer (C) is too large, the percentages of the other monomers become relatively small and resistance to washing tends to be poor. Therefore, the percentage of Monomer (C) is 70 wt% or less and, preferably, 60 wt% or less.

[0341] Also, when the copolymer, which comprises Monomer (D) together with Monomers (A) to (C) as constitutive monomers, is treated, smoothness and good texture can be given to fiber and moist feeling of use can be obtained. However, in the case where Monomer (D) is too much water-repellency, resistance to washing and the like are inferior because hydrophilic nature of the coating become high by amine portion contained in Monomer (D). The percentage of Monomer (D) is 1 to 100 wt% and, preferably, 5 to 50 wt% with respect to a whole amount of Monomers (A) to (C).

[0342] Although a concentration of the copolymer is not restricted in particular, it is preferably 0.1 to 10 wt% and, more preferably, 1 to 5 wt%. In the case where the amount of the copolymer is too little, the sufficient effect can not be obtained at once treatment. On the contrary, applicability, spreadability, feeling of use and the like become inferior and flaking may be caused in the case where the amount is too much.

[0343] The other ingredients can be comprised into the water-repellent or treatment for fiber of the present invention within the range that the effect of the present invention is not spoiled. Also, it is possible to form a colored coat having water-repellency when coloring materials such as pigment or dye are comprised therein. On the other hand, it is possible to prevent discoloring of the material to be treated when an ultraviolet absorber is comprised therein.

5 [0344] As for the material to be treated with the water-repellent and treatment for fiber of the present invention, fibrous materials having optional forms such as single fiber, spun yarn, random fiber, fabric and a final product are preferable. Such the final product can be, for example, shoes, an umbrella, a hat or cap, a ski suit, a shirt or a carpet. In the present invention, the fibrous material also includes leather, the other fibrous materials and products thereof such as fiber of paper or paper products. Also, in addition to the fibrous material, it is possible to treat the other materials such as glass
10 plates, glass products, metal plates or metal products, that water-repellency and unsusceptibility to fouling are required thereto.

[0345] As a method for applying the water-repellent and treatment for fiber of the present invention, known methods, e.g., dipping method, roll coating method or spray method, may be used. Of course, instruments such as brush or comb can be used properly as occasion demands.

15 [0346] One of the most simple treatment method in the present invention can be, for example, the method that the material to be treated is dipped into or sprayed with a solution of the copolymer of the present invention and then the material is, optionally with squeezing, dried naturally or with heating. Also, in clothes such as a shirt, a method that the solution of the copolymer is sprayed on the cloth before ironing and then the cloth is pressed by iron or steam iron, is preferable.

20 [0347] Lastly, a synthetic example of the copolymer in accordance with the present invention is described.

Synthetic Examples 1 to 24

25 [0348] In order that each of Monomers (A) to (D) has a ratio described in TABLE 43, the mixture of the monomers was dissolved into 100 ml of ethanol with the preparation amount. The solution was heated with stirring under nitrogen gas stream for 1 hour at 70°C. 0.05g of potassium persulfate was added to the solution and the mixture was reacted overnight. The reaction mixture was cooled down to room temperature and concentrated under a vacuum. The residue was dissolved into 10ml of ethanol and the solution was added to 500ml of n-hexane. The deposits were collected to give the aimed copolymer.

TABLE 43

Synthetic Examples	Monomer (parts by weight)							Preparation Amount (g)	Yield (%)
	A2	B1	C1	C2	C3	C4	D1		
1	5	1	4	-	-	-	-	20	97.5
2	5	1	2	-	-	-	-	16	96.9
3	5	1	-	4	-	-	-	20	98.5
4	5	1	-	1	-	-	-	14	100.0
5	5	3	-	1	-	-	-	18	98.9
6	12	7	-	1	-	-	-	20	97.5
7	9	10	-	1	-	-	-	20	92.5
8	2	1	-	1	-	-	-	20	98.5
9	5	1	-	-	4	-	-	20	99.0
10	12	7	-	-	1	-	-	20	97.0
11	9	10	-	-	1	-	-	20	95.0
12	5	1	-	-	-	4	-	20	99.0
13	5	3	-	-	-	1	-	20	97.5
14	12	7	-	-	-	1	-	20	98.5
15	9	10	-	-	-	1	-	20	94.5
16	2	1	-	-	-	1	-	20	97.5

TABLE 43 (continued)

Synthetic Examples	Monomer (parts by weight)							Preparation Amount (g)	Yield (%)
	A2	B1	C1	C2	C3	C4	D1		
17	12	7	-	-	1	2	-	20	97.0
18	12	7	-	-	-	1	2	20	99.5
19	12	7	-	-	-	1	4	22	90.9
20	12	2	-	-	-	6	2	22	91.4
21	12	2	-	-	-	6	4	24	96.7
22	12	4	-	-	-	4	2	22	90.0
23	12	4	-	-	-	4	4	24	91.3
24	4	8	-	8	-	-	-	20	91.0

[0349] Figs. 2 to 5 each show NMR spectral data of the copolymer that was obtained by Synthetic Examples 6, 10, 12 and 18, respectively. In these NMR spectral data (solvent CDCl_3 or $\text{DMSO}-d_6$) of the resulting copolymer, the peak of hydrogen atom of $\text{CH}_2=\text{C}$ derived from the monomer used as a starting material, that the peak should be observed in 6-7 ppm or near, was not observed. As a result, generation of the copolymer was confirmed. Also, in the present invention, generation of the other copolymers was confirmed in the similar manner.

Synthetic Example 25

[0350] 10.00g of Monomer A1 and 2.02g of Monomer B1 were dissolved into 100ml of ethanol and the solution was heated with stirring under nitrogen gas stream for 1 hour at 70°C. 0.05g of dimethyl 2,2-azobis(isobutyrate) was added to the solution and the mixture was heated with stirring for 24 hours at 70°C. The reaction mixture was cooled down to room temperature and concentrated under a vacuum. The residue was dissolved into 10ml of ethanol and the solution was added to 500ml of n-hexane. The deposits were collected to give 11.50g (yield 95.7%) of the aimed copolymer.

Synthetic Example 26

[0351] 10.00g of Monomer A2 and 5.00g of ethyl methacrylate were dissolved into 100ml of ethanol and the solution was heated with stirring under nitrogen gas stream for 1 hour at 70°C. 0.05g of 2,2-azobisisobutyronitrile was added to the solution and the mixture was heated with stirring for 24 hours at 70°C. The reaction mixture was cooled down to room temperature and was concentrated under a vacuum. The residue was dissolved into 10ml of ethanol and the solution was added to 500ml of n-hexane. The deposits were collected to give 14.20g (yield 94.7%) of the aimed copolymer.

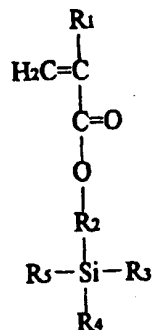
Synthetic Example 27

[0352] 18.95g (yield 94.8%) of the aimed copolymer was obtained by the same process as in Synthetic Example 25, except for using 10.00g of Monomer A1 and 10.00g of Monomer B1.

Claims

1. A composition comprising a copolymer containing silyl groups wherein each silyl groups has at least one reactive functional group bonded thereto.
2. A composition according to claim 1, wherein said copolymer comprises, as one of constitutive monomers, Monomer (A) shown by the following Formula (I):

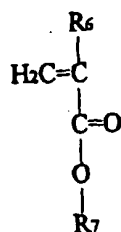
Formula (I)



wherein R_1 is a hydrogen atom or methyl group; R_2 is an alkylene group having 1-6 carbon atoms; and R_3 , R_4 and R_5 each is a reactive functional group which can cross-link molecules of the copolymer by hydrolyzing.

3. A composition according to claim 1 or 2, wherein said copolymer further comprises, as one of constitutive monomers, Monomer (B) shown by the following Formula (II):

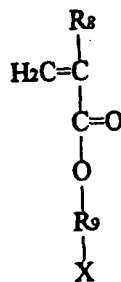
Formula (II)



wherein R_6 is a hydrogen atom or methyl group; and R_7 is an alkyl group having 1-18 carbon atoms.

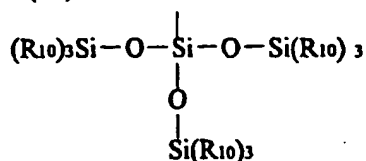
4. A composition as in any of claims 1 to 3, wherein said copolymer further comprises, as one of constitutive monomers, Monomer (C) shown by the following Formula (III):

Formula (III)



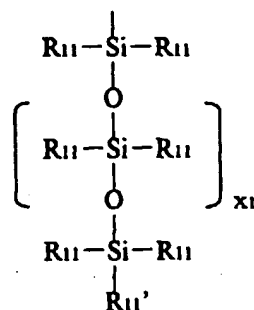
wherein R_8 is a hydrogen atom or methyl group; R_9 is an alkylene group having 1-6 carbon atoms; and X is a group expressed by any of the following Formulae (IV) to (VI):

Formula (IV)



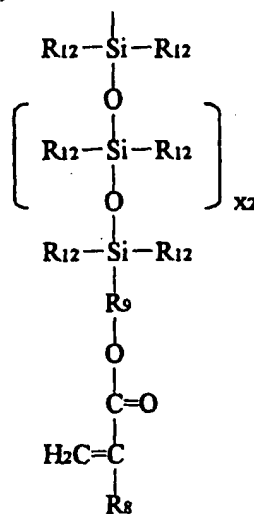
wherein R_{10} is an alkyl group having 1-6 carbon atoms;

Formula (V)



wherein R_{11} and R_{11}' each is an alkyl group having 1-6 carbon atoms; and x_1 is an integer of positive number; and

Formula (VI)



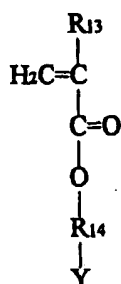
wherein R_8 and R_9 are the same as defined in Formula (III); R_{12} is an alkyl group having 1-6 carbon atoms; and x_2 is an integer of positive number.

5. A composition as in any of claims 2 to 4, wherein the percentage of Monomer (A) is 25 to 99 wt% in the copolymer.
6. A composition as in any of claims 3 to 5, wherein the percentage of Monomer (B) is 1 wt% or more in the copolymer.
7. A composition as in any of claims 4 to 6, wherein the percentage of Monomer (C) is 1 wt% or more in the copolymer.

mer.

8. A composition as in any of claims 1 to 7, wherein said copolymer further comprises, as one of constitutive monomers, Monomer (D) shown by the following Formula (VII):

Formula (VII)



- wherein R_{13} is a hydrogen atom or methyl group; R_{14} is an alkylene group having 1-6 carbon atoms; and Y is a group expressed by $-N^+(R_{15})_3$ or $-N(R_{15})_2$, wherein R_{15} is an alkyl group having 1-6 carbon atoms.
9. A composition according to claim 8, wherein the percentage of Monomer (D) is within the range of 1 to 100 wt% with respect to a whole amount of Monomer (A), Monomer (B) and Monomer (C) in the copolymer.
10. A composition as in any of claims 2 to 9, wherein each of R_3 , R_4 and R_5 is an alkoxy group having 1-6 carbon atoms.
11. A cosmetic for coating, which is the composition according to any of claims 1 to 10.
12. A cosmetic for modifying the nature of hair, which is the composition according to any of claims 1 to 10.
13. A composition as in any of claims 1 to 10, which is a hair color further comprising a pigment and/or an acidic dye.
14. A composition as in any of claims 1 to 10, which is a cosmetic further comprising a pigment and/or an acidic dye.
15. A composition as in any of claims 1 to 10, which is a make-up cosmetic further comprising a pigment and/or an acidic dye.
16. A cosmetic preparation as in any of claims 11 to 15, wherein a siliconized polysaccharide is further comprised.
17. A cosmetic pack, which is the composition according to any of claims 1 to 10.
18. A water-repellent, which is the composition according to any of claims 3 to 10.
19. A water-repellent according to claim 18, wherein the percentage of Monomer (A) is 25 to 85 wt% in the copolymer.
20. A water-repellent according to claim 18 or 19, wherein the percentages of Monomer (B) and Monomer (C) are 5 wt% or more and 1 wt% or more in the copolymer, respectively.
21. A treatment for fiber, which is the composition according to any of claims 3 to 10.
22. A treatment for fiber according to claim 21, wherein the percentage of Monomer (A) is 25 to 85 wt% in the copolymer.
23. A treatment for fiber according to claim 21 or 22, wherein the percentages of Monomer (B) and Monomer (C) are 5 wt% or more and 1 wt% or more in the copolymer, respectively.

24. A copolymer comprising Monomer (A) of said Formula (I), Monomer (B) of said Formula (II) and Monomer (C) of said Formula (III) as constitutive monomers.
- 5 25. A copolymer comprising Monomer (A) of said Formula (I), Monomer (B) of said Formula (II), Monomer (C) of said Formula (III) and Monomer (D) of said Formula (VII) as constitutive monomers.
26. A copolymer according to claim 24 or 25, wherein each of R_3 , R_4 and R_5 is an alkoxy group having 1-6 carbon atoms.
- 10 27. A coat-forming method comprising a step of es hydrolyzing the composition according to any of claims 1 to 23 on a material to be treated to cross-link molecules of the copolymer.
28. A coat-forming method according to claim 27, wherein said composition is the cosmetic according to any of claims 11 to 16 and the material to be treated is human hair or epidermis.
- 15 29. A coat-forming method according to claim 27, wherein said composition is the water-repellent according to any of claims 18 to 20 and the material to be treated is fiber, paper or glass.
30. A coat-forming method according to claim 27, wherein said composition is the treatment for fiber according to any of claims 21 to 23 and the material to be treated is fiber.
- 20 31. A method for pack comprising steps of: hydrolyzing the cosmetic pack according to claim 17 on skin to cross-link molecules of the copolymer; and peeling the cosmetic pack from the skin after drying.

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Fig. 1

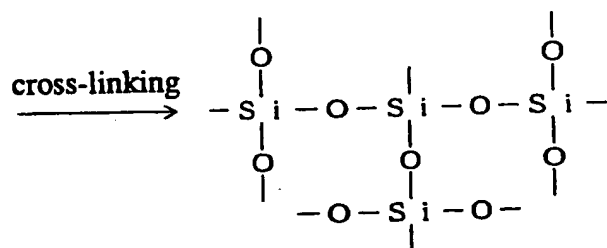
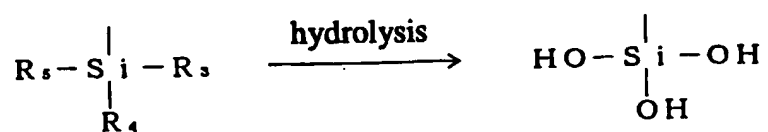
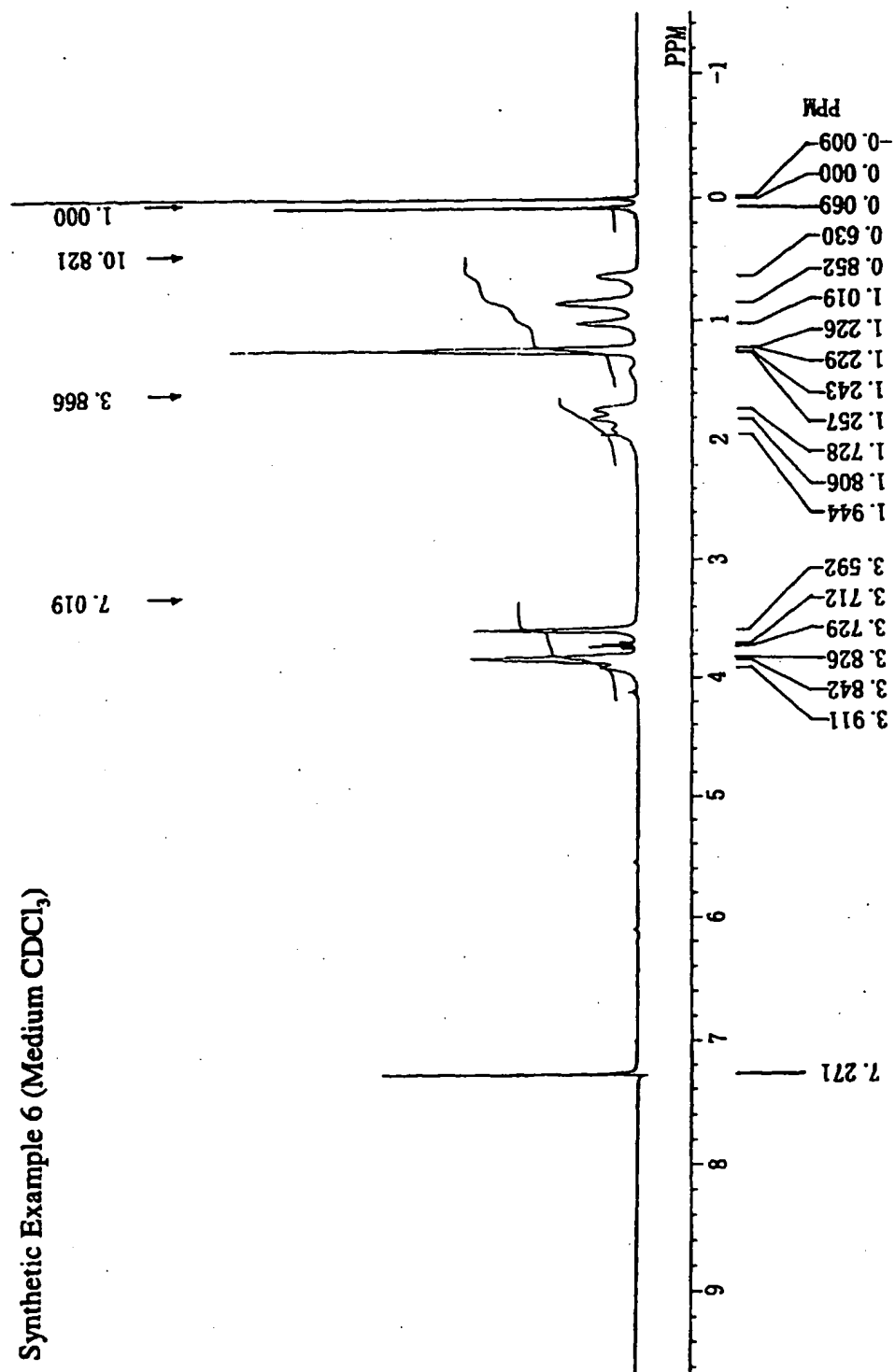
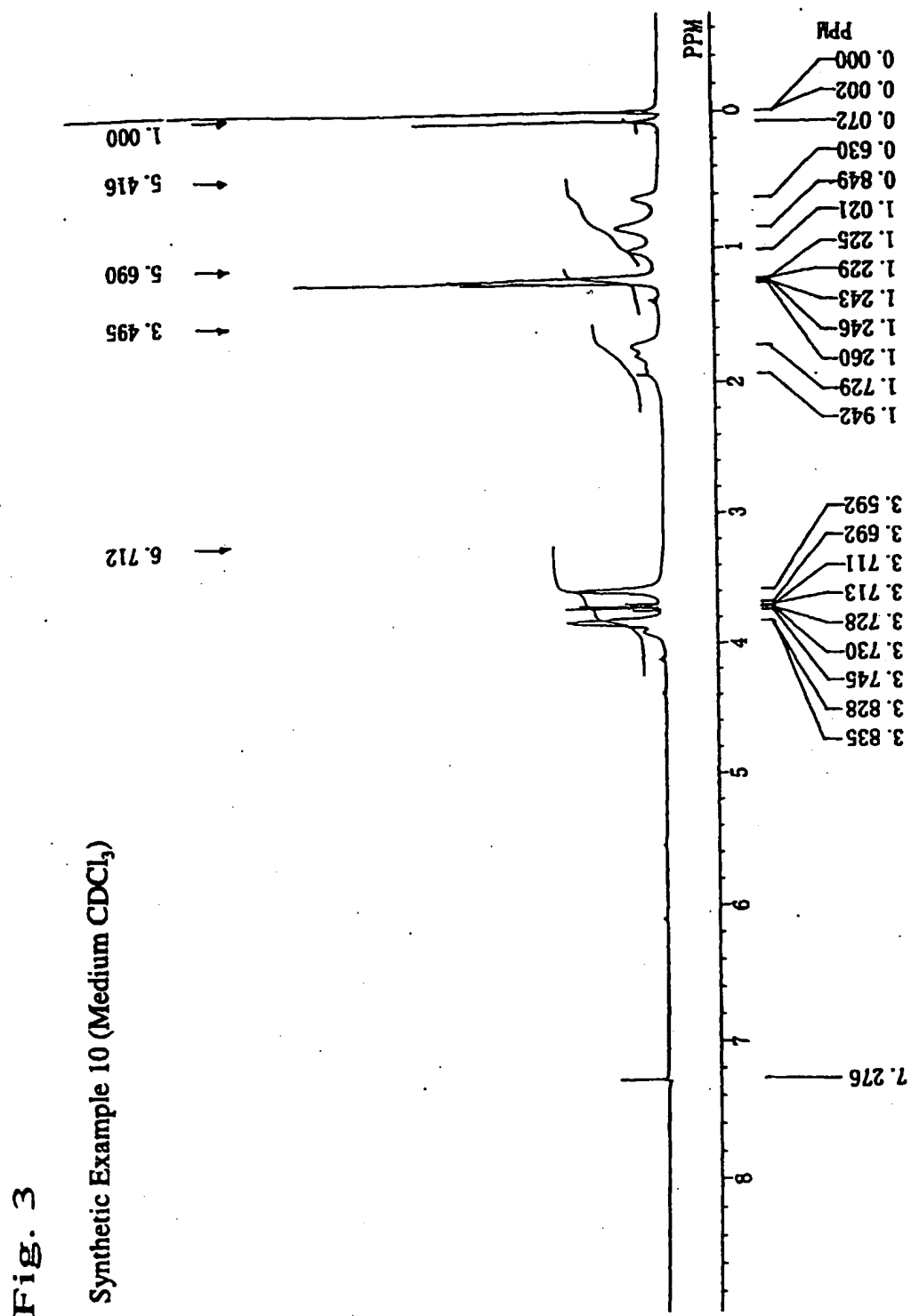


Fig. 2

Synthetic Example 6 (Medium CDCl₃)



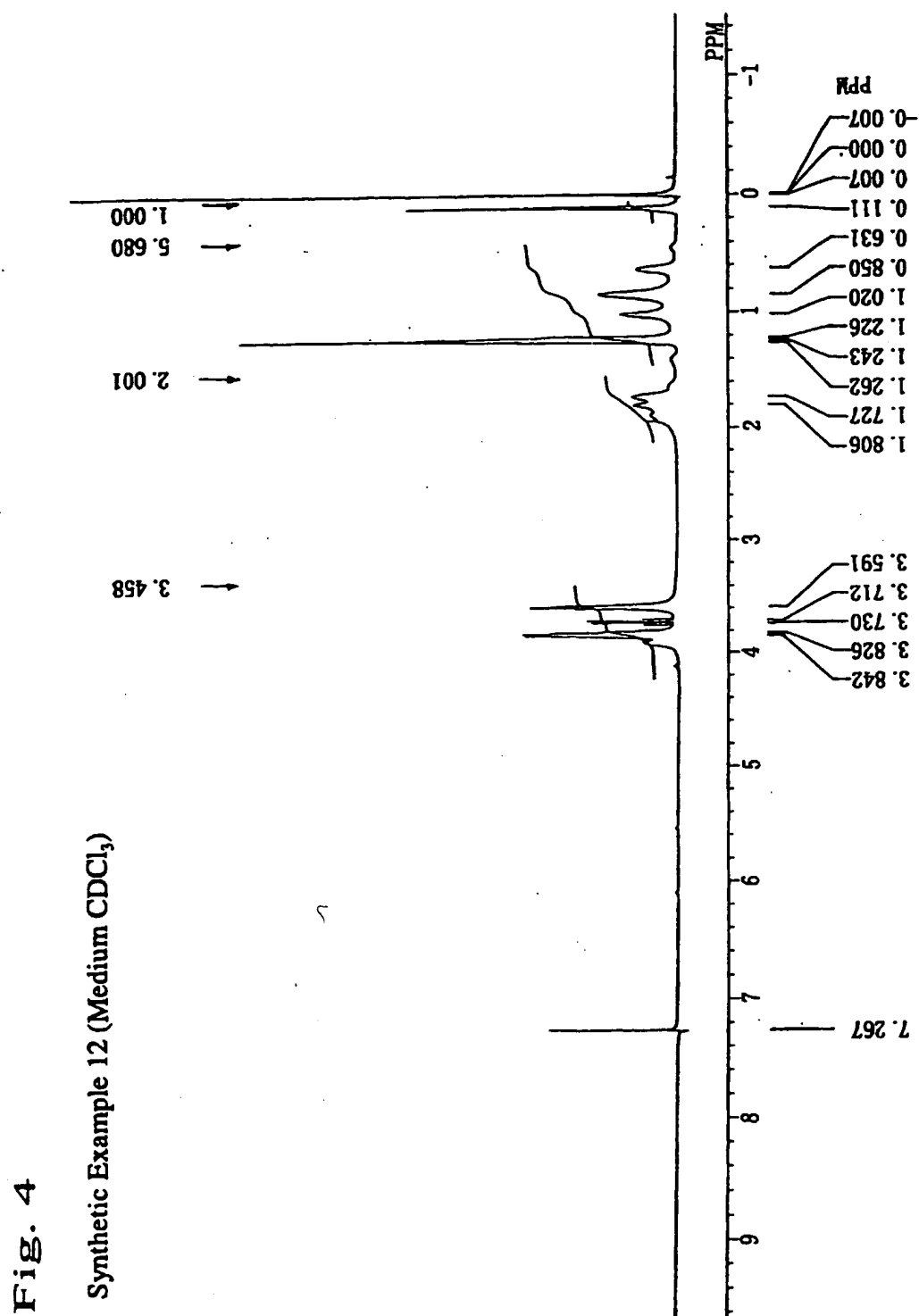
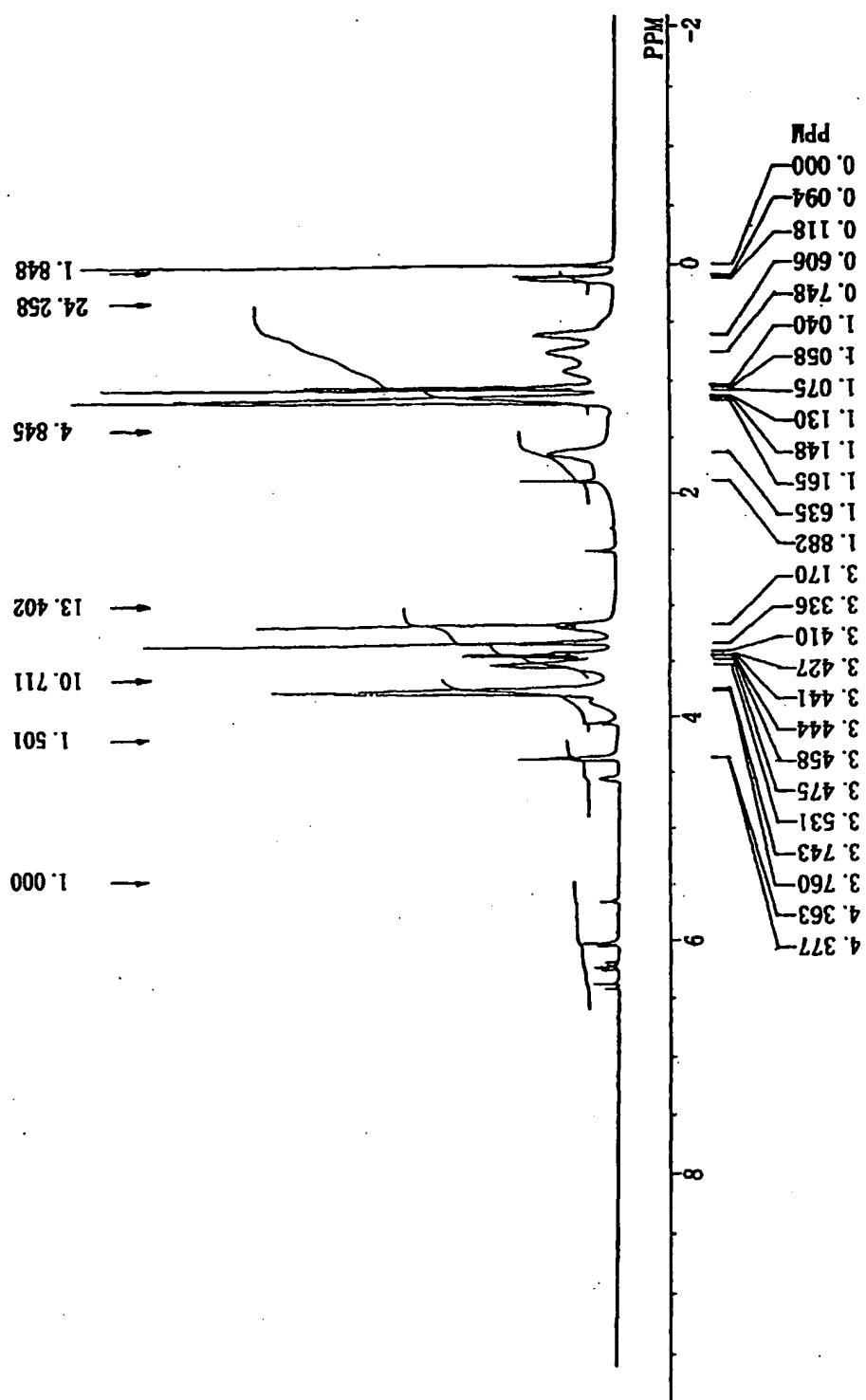


Fig. 5

Synthetic Example 18 (Medium DMSO-d₆)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP98/02407

A. CLASSIFICATION OF SUBJECT MATTER Int.Cl ⁸ C08L43/04, C08L83/07, C08L33/06, C08L33/14, C08F30/08, C08F20/10, C08F20/34, C08F290/06, C08G77/20, A61K7/00, According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) Int.Cl ⁸ C08L43/04, C08L83/07, C08L33/06-33/14, C08F30/08, C08F20/10, C08F290/06, C08G77/20, A61K7/00-A61K7/48, C09K3/18, D06M15/643, Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP, 8-12901, A (Kanebo-NSC Ltd.), 16 January, 1996 (16. 01. 96), Claims & EP, 690109	1-7, 10, 24, 26-27
X	JP, 3-128312, A (The Procter & Gamble Co.), 31 May, 1991 (31. 05. 91), Claims & EP, 412707	1-12, 14, 24-28
X	JP, 6-166613, A (Kanebo-NSC Ltd.), 14 June, 1994 (14. 06. 94), Claims (Family: none)	1-3, 5-6, 8-11, 14-15, 27
X	JP, 6-9332, A (Kose Corp.), 18 January, 1994 (18. 01. 94), Claims (Family: none)	1, 3-4, 6-7, 11 14-15, 27-28
X	JP, 4-321618, A (Osaka Organic Chemical Industry Ltd.), 11 November, 1992 (11. 11. 92), Claims (Family: none)	1-3, 5-7, 10-12, 27-28
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed		"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family
Date of the actual completion of the international search 4 September, 1998 (04. 09. 98)		Date of mailing of the international search report 16 September, 1998 (16. 09. 98)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
Facsimile No.		Telephone No.

Form PCT/ISA/210(second sheet)(July 1992)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP98/02407

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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X	JP, 8-253539, A (Mitsubishi Chemical Corp.), 1 October, 1996 (01. 10. 96), Claims (Family: none)	1, 3-4, 6-12, 14, 27-28
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X	JP, 5-17324, A (Osaka Organic Chemical Industry Ltd.), 26 January, 1993 (26. 01. 93), Claims (Family: none)	1, 3-4, 6-9, 11-12, 27-28
X	JP, 59-203738, A (Nippon Shokubai Kagaku Kogyo Co., Ltd.), 17 November, 1984 (17. 11. 84), Claims (Family: none)	1-3, 5-6, 10, 21-27, 30
X	JP, 2-8285, A (Kansai Paint Co., Ltd.), 11 January, 1990 (11. 01. 90), Claims & EP, 348946	1-2, 5, 8-10, 18-19, 27, 29
X	JP, 9-328677, A (NOF Corp.), 22 December, 1997 (22. 12. 97), Claims (Family: none)	1, 3-4, 6-7, 18-19, 27, 29
X	JP, 5-214676, A (Dainippon Ink & Chemicals, Inc.), 24 August, 1993 (24. 08. 93), Claims (Family: none)	1, 3-4, 6-7, 18, 20, 27, 29
X	JP, 5-239435, A (Osaka Organic Chemical Industry Ltd.), 17 September, 1993 (17. 09. 93), Claims (Family: none)	1-3, 6, 10, 18, 27
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A. (Continuation) CLASSIFICATION OF SUBJECT MATTER

A61K7/48, C09K3/18, D06M15/643, D06M13/513

B. (Continuation) FIELDS SEARCHED

D06M13/513